ACID ACTIVATION OF BLEACHING EARTH FOR CRUDE PALM OIL TREATMENT

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ABSTRACT

The unique properties of clay and clay minerals caused them to be valuable in a wide range of industrial applications. Low cost, availability and effectiveness are the prevailing factors that promoted clay and clay minerals to be used extensively as adsorbents in the purification of vegetable oils. The main objective of this study is to produce new types of activated clay by hydrofluoric acid activation and modify the surface physical of hydrofluoric acid activated clays in order to enhance their bleaching performance. Experiments were divided into two parts. In part 1, montmorillonite clay was activated with hydrofluoric acid (HF) and sulphuric acid (H_2SO_4) at 90^oC using a range of activation times of 1, 3, 5, and 7 hours, and at various acid concentrations of 2, 3, 4, 5, and 6 M. The structure and surface texture of the prepared materials were characterised by X-ray fluorescence spectrometer (XRF), X-ray diffraction (XRD), Fourier Transmittance Infrared (FTIR), BET surface area and Scanning electron microscope (SEM). Results indicated that increasing the acid concentration and activation time, increases the dissolving rate of octahedral cations (Mg, Fe and Al). They also showed that the clay activated with HF has the highest dissolution, followed by H_2SO_4 activated clay and then the natural clay sample. Therefore, activation with sulphuric and hydrofluoric acid caused structural changes in the activated clay samples. In addition, the specific surface areas in the acid activated clays are larger than the natural clay. The specific surface areas in acid activated clays also increase several times as the acid concentration and activation time increases. In part 2, a study was carried out with the intention to assess and compare the bleaching performance of the acid activated clay with that of the natural clay and commercial activated clay, and also to investigate the effect of the activation parameters, namely acid concentration and activation time. The effects of acid concentration and activation time on the bleaching

performance were evaluated by determining the percentage (%) of Lovibond red colour index. Results revealed that, for the same amount of bleaching clay, the percentage removal of free fatty acids, red colour index, peroxide value and phosphorus content appeared higher in the sample that activated with H_2SO_4 and HF. On the other hand, the clay activated with HF gave the best results in terms of retaining the original carotene content of the oil. The results showed that, HF activated clay has almost similar carotene content as the original crude palm oil. This might imply that HF activated clay is a good candidate to be used as an adsorbent in the purification of palm oil. Nevertheless, it was shown that the clays activated with 5 M H_2SO_4 and 3 M HF at 1 hour activation time were appropriate adsorbents for the purification of palm oil. At these conditions, these clays produced oils with the least free fatty acid and peroxide value as well as with the best red colour index removal.

ABSTRAK

Sifat-sifat unik tanah liat dan mineral tanah liat telah menjadikan ia sangat berguna untuk pelbagai kegunaan industri. Kos yang rendah, mudah didapati serta keberkesanan merupakan faktor-faktor utama yang menjadikan tanah liat dan mineral tanah liat digunakan secara meluas sebagai zat penjerap di dalam penulenan minyak sayuran. Objektif utama kajian ini adalah untuk mengubah ciri-ciri fiziko-kimia permukaan tanah peluntur bagi tujuan mempertingkatkan lagi keupayaan penjerapannya. Ujikaji ini dibahagikan kepada dua bahagian. Dalam bahagian 1, tanah liat montmorilonite diaktifkan oleh asid sulfurik (H_2SO_4) dan asid hidroflorik (HF) pada suhu 90^oC dalam masa pengaktifan (1, 3, 5, 7 jam) dan pada pelbagai kepekatan asid (2, 3, 4, 5, 6 M). Pencirian struktur dan tekstur permukaan mineral tanah liat dianalisis oleh spektrometer pendarfluor sinar-X (XRF), belauan sinar-X (XRD), luas permukaan BET dan mikroskop pengimbas elektron (SEM). Keputusan menunjukkan bahawa peningkatan kepekatan asid dan masa pengaktifan akan meningkatkan kadar kelarutan kation oktahedron (Mg, Fe and Al), dan tanah liat yang diaktifkan dengan HF mempunyai kelarutan yang tertinggi, diikuti oleh H_2SO_4 dan seterusnya, sampel tanah liat yang tidak diaktifkan. Hasil kajian menunjukkan bahawa peningkatan dalam kepekatan asid dan masa pengaktifan, kadar penyingkiran kations octahedral (Mg, Fe dan Al) juga meningkat. Ini juga menunjukkan bahawa tanah liat yang diaktifkan dengan HF mempunyai kadar penyingkiran yang tinggi, diikuti dengan tanah liat diaktifkan dengan sulfurik asid dan sampel tanah liat semulajadi. Oleh itu, pengaktifan dengan sulfurik dan hidroflorik asid menyebabkan perubahan struktur dalam sampel tanah liat yang diaktifkan. Keluasan permukaan spesifik dalam asid tanah liat diaktifkan juga meningkat beberapa kali apabila kepekatan asid dan masa pengaktifan meningkat.

Dalam bahagian 2, satu kajian telah dijalankan dengan tujuan untuk menilai dan membandingkan prestasi pelunturan tanah liat asid diaktifkan dengan tanah liat semulajadi dan tanah liat komersial diaktifkan, dan juga untuk mengkaji kesan parameter pengaktifan, iaitu kepekatan asid dan masa pengaktifan. Kesan kepekatan asid dan masa pengaktifan kepada prestasi pelunturan dinilai dengan menentukan peratusan (%) Lovibond indeks merah penyingkiran warna. Hasil kajian menunjukkan bahawa, pada jumlah pelunturan tanah liat yang sama, penyingkiran peratusan asid lemak bebas, warna indeks merah, nilai peroksida dan kandungan fosforus didapati lebih tinggi dalam sampel yang diaktifkan dengan H_2SO_4 dan HF. Sebaliknya, tanah liat diaktifkan dengan HF memberikan hasil yang terbaik dari segi mengekalkan kandungan karotena asal minyak. Hasil kajian menunjukkan bahawa, HF diaktifkan tanah liat mempunyai kandungan karotena yang hampir sama dengan minyak sawit mentah yang asal. Ini mungkin membayangkan bahawa HF diaktifkan tanah liat adalah calon yang baik untuk digunakan sebagai bahan penjerap dalam pemurnian minyak sawit. Walau bagaimanapun, ia telah menunjukkan bahawa tanah liat diaktifkan dengan 5 M H_2SO_4 dan 3 M HF pada masa pengaktifan 1 jam adalah penjerap yang sesuai untuk pembersihan minyak sawit. Pada keadaan ini, minyak yang telah dirawat dengan tanah liat ini menghasilkan kurang asid lemak bebas dan nilai peroksida serta indeks merah penyingkiran warna terbaik.

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LIST OF SYMBOLS

α	Alpha
β	Beta
g	Gram
h	Hours
kg	Kilogram
M	Molarity
meq	Milliequivalent
N	Normality of solution
Θ	Diffraction angle
ppm	Parts per million
P/P_o	Relative pressure
S_{BET}	Specific surface area (m^2g^{-1})

LIST OF ABBREVIATIONS

BPO	Bleached palm oil
BET	Brunauer, Emmett and Teller
CPO	Crude palm oil
FFA	Free fatty acid
FTIR	Fourier Transform Infrared
HCl	Hydrochloric acid
HF	Hydrofluoric acid
HNO_3	Nitric acid
H_2SO_4	Sulphuric acid
IPA	Isopropyl alcohol
PORIM	Palm Oil Research Institute of Malaysia
KOH	Potassium hydroxide
NaOH	Sodium hydroxide
pH	Potential hydrogen
PV	Peroxide value
SEM	Scanning electron microscope
SiO_2	Silica oxide

UV-Vis	Ultraviolet-visible
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

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CHAPTER 1

INTRODUCTION

1.1 Background

The process of refining is an essential step in the production of vegetable oils and fats. There are basically two types of refining processes available in the vegetable oil industry, namely; chemical and physical refining (Rossi et al., 2003; Valenzuela-Diaz & Souza-Santos, 2001). These processes differ in the type of chemicals used and the mode by which the free fatty acids (FFA) are removed (Morad et al., 2001). A refining process comprises of several stages such as degumming, neutralization, bleaching and deodorization (AL-Zahrani & Daous, 2000). Among the four stages, bleaching is the most critical stage since it helps to improve the colour, flavour, taste and stability of the final oil products (Rossi et al., 2003; Tsai et al., 2003; Foletto et al., 2006; Nguetnkam et al., 2008).

The bleaching process is carried out using different types of adsorbents. The most extensively used adsorbent is bleaching earth (Hymore, 1996; Bayrak, 2003; Gulsah et al., 2006; Joy et al., 2007; Woumfo et al., 2007). Other adsorbents that have been tested for the removal of pigment and impurities from vegetable oils include activated carbon and silica-based products (Joy et al., 2007; Wu & Li, 2009). However, bleaching earth is the most preferred due to its relatively high adsorption performance for coloured materials and low purchase cost (Wu & Li, 2009; Liu et al., 2008). Bleaching earth improves the quality of the oil and reduces the tint of any coloured oil to a lighter shade by changing the basic colour units in the oil without altering the chemical properties of the oil (Okwara & Osoka, 2006). It is also responsible for the removal of pigments and other impurities, such as soap, trace metals, phospholipids, oxidation products and polyaromatics (Rossi et al., 2003; Bayrak, 2003; Zschau, 1987; Kaynak et al., 2004;

Temuujin et al., 1951; Wei et al., 2004; Lin & Yoo, 2007). Bleaching earth has been used in refining vegetable oils since the end of the 18th century (Beneke & Lagaly, 2002). To date, bleaching earth or bleaching clay, which is also known as fuller's earth, is the most extensively used agent in the bleaching process (Sabah, 2007; Sabah & Majdan, 2009).

In order to enhance the chemical and physical properties of bleaching earth, activation is required, and the most commonly used techniques are acidic, basic, organic or heat treatment (Babaki et al., 2008; Gunawan et al., 2010). During these treatments, the structure and textural properties of the clay and clay minerals are altered in a controlled environment to enhance the specific properties of bleaching earth (Valenzuela-Diaz & Souza-Santos, 2001). Activation of bleaching earth by acid treatment is by far the most studied technique due to its simplicity and the fact that it is a proven method, which has been used extensively for the past several decades. Today, this technique remains as one of the most widely used chemical modification techniques for the refining of vegetable oils. There are diverse types of acids used for acid activation, such as sulphuric, hydrochloric, nitric and acetic acids (Hussin et al., 2011). Sulphuric (H_2SO_4) and hydrochloric (HCl) acids are probably the most extensively used acids in acid activation. Within conventional vegetable oil refining process parameters, these two acids show strong affinity for the undesirable components (Valenzuela-Diaz & Souza-Santos, 2001; Siddiqui, 1968). Unfortunately, these types of acid-activated clays result in relatively lower levels of carotene content in the bleached and refined palm oil.

In an effort to prevent these losses, hydrofluoric acid (HF) was chosen particularly because of its additional properties, which are not available in H_2SO_4 and HCl. To date, the possibility of acid activation using hydrofluoric acid to bleach the palm oil has never

been examined. Therefore, HF was used in this work as an activating agent for K-10 montmorillonite clay in order to improve the effectiveness of bleaching process in the palm oil processing. Throughout this work, sulphuric acid activation was used as a benchmark for comparison with the results obtained from hydrofluoric acid.

1.2 Problem Statement

It is well known that the majority of the carotenoids in palm oil are destroyed in the refining process, which is used to produce of light coloured oils. This phenomenon causes the loss of a natural source of carotenoids (Rossi et al., 2001). Crude palm oil has a rich orange-red colour due to its high carotene content, which varies between 500-700 ppm. The major types of carotenoids in crude palm oil are α- and β-carotenes, which account for 90% of the total carotenes in palm oil. β-carotene is the most important type as it is a precursor of vitamin A (Choo et al., 1991; Sundram et al., 2003). It plays a significant role in the prevention of various illnesses such as pancreatic cancer and gastric cancer, and degenerative diseases such as heart disease as it enhances the immune response (Sundram et al., 2003; Bendich, 1989; Murakoshi et al., 1989). Therefore, it is important to retain the β-carotene content in the bleached or refined oil and reduce its losses during the refining process. Commercial acid-activated clays resulting in high carotene content loss after the refining process. Therefore, there is a need to develop a new activated bleaching material. In general, acid activation by HF results in an increased number of acid centers. Hence, the changes in clay structure caused by fluorination are accompanied by an increase in the surface area and porosity, mainly in the meso and macropore range. Treatment of clays with F^- ions could result in changes in the texture and strength of the surface acidic sites produced, through anionic exchange, when the surface -OH groups are substituted by the more electro negative F^- anion, and the subsequent protonisation of vicinal OH^-s (Belzunce et al., 1998). In

theory, the use of HF as an activating agent is an attempt to modify the pore structure and/or the surface properties of the clay minerals.

1.3 Objectives

The objectives of this research are:

a) To produce new types of activated clay by HF activation at different acid concentrations and times.
b) To characterise the physical and chemical properties of HF activated clays at different acid concentration and times and compare them with the properties of H_2SO_4 activated clays.
c) To investigate the HF and H_2SO_4 activated clays performance on physico-chemical properties of the bleached palm oil by assessing the free fatty acids, peroxide value, phosphorus, Lovibond colour and carotene content.
d) To compare the bleaching performance of the HF and H_2SO_4 activated clays with that of the natural clay and commercial activated clay.

1.4 Scope of work

Basically, this study is divided into two parts. In part 1, K-10 montmorillonite clay is selected as the raw material. This is due to its unique properties such as large specific surface area, chemical and mechanical stability, swelling capacity, high cation exchange capacity and high adsorption capacity (Konta, 1995). Nevertheless, the application of these clays in the purification of vegetable oils has received relatively little attention in the literature. In order to modify the physical and surface chemical properties of the bleaching clay, acid treatment technique is used. The structure and surface texture of acid activated clay are then characterised. In part 2, physical refining method is carried out to assess the bleaching performance of the acid activated clays. Free fatty acid,

peroxide value, phosphorus content, Lovibond colour and β-carotene content of the bleached palm oil are evaluated. Finally, the bleaching performance of acid activated clays is compared with that of the natural clay and commercial activated clay.

1.5 Structure of Thesis

Overall, this thesis consists of five main chapters. These chapters are Introduction, Literature Review, Research Methodology, Results and Discussion, and Conclusions.

Chapter 1: Introduction

This chapter includes the background relevant to this work, a brief introduction of the work done in this research, objectives of research, the scope of work and the structure of this thesis.

Chapter 2: Literature review

This chapter reviews the previous work done related to this study. It focuses on the bleaching clay performance which covers the textural characteristics and surface chemistry. The chapter includes discussion on the characteristics of porous volume, structure of clay minerals and the active sites of clay minerals. The review also covers several modification methods of the bleaching clay including modification by acid, base, organic, heat and microwave.

Chapter 3: Research Methodology

This chapter presents the experimental set up and the procedures of the work done in this study. It starts with the description of the experimental rig and followed by the experimental procedures of preparing the acid activated clays and the bleaching process.

Chapter 4: Results and Discussion

This chapter discusses the results obtained from the methods approached and the analysis of these results.

Chapter 5: Conclusion and recommendation

Chapter 5 presents the conclusion of this study. All the work carried out and its results are summarised in this chapter. In addition, this chapter also includes the recommendations and suggestions that can be used as a guidance for future researchers who are interested to do research in this area.

CHAPTER 2

LITERATURE REVIEW

2.1 Clay and Clay Minerals

There are numerous books and reviews about clay and clay minerals, as well as their applications. They are essential to our current understanding of how and why clay minerals have such an extensive industrial utilisation (Murray, 1999). This sub-chapter provides a general description of the clay and clay minerals as well as some of the important applications related to the bleaching earth.

The term clay and clay minerals are considered very different in its context. Because of that, the Association Internationale pour l'Etude des Argiles (AIPEA) nomenclature committee for 2006 has summarised some recommendations of nomenclature for minerals, phyllosilicates, clays and clay minerals. The AIPEA has defined clay as "a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired" (Guggenheim et al., 2006). The definition of clay minerals according to the AIPEA refers to "phyllosilicate minerals and minerals which impart plasticity to clay which harden upon drying or firing" (Guggenheim et al., 2006). Clay and clay minerals have been used extensively as low-cost adsorbents for diverse applications, such as adsorbents in the bleaching of edible oils, medications, fertilizers, catalyst beds, carbonless copy paper, textiles, petroleum refining, etc. (Korichi et al., 2009; Babaki et al., 2008; Murray, 1999) . Table 2.1 shows some of the industrial uses of clay minerals.

Table 2.1: Physical characteristics and industrial uses of clay minerals (adapted from Murray, 1999)

Clay minerals	Physical Characteristics	Industrial applications
Kaolin	White or near-white in colour Very limited substitutions Minimal charge on the layer Very low cation exchange capacity Relatively low surface area Low absorption capacity	Adhesives, cement, ceramic, cosmetics, cracking catalysts, crayon and chalk, enamels, extender pigment in ink, extender pigment in paint, fertilizers, fiberglass, filler in plastics, filler in rubber, foundries, fruit and vegetable protection, insecticide and pesticide carriers, medicines and pharmaceuticals, paper coating, paper filling, pencil lead, polishing compounds, roofing granules, soaps and detergents, tanning leather, textiles.
Smectite	Variable colour, usually tan or greenish-gray Considerable lattice substitutions High layer charge Medium to high cation exchange capacity Very high surface area High absorption capacity	Adhesives, aerosols, agricultural carriers, animal feel bonds, barrier clays, bleaching clays, cat litter, catalysts, cement, ceramics, cosmetics, crayons, de-inking of paper, desiccants, detergents, drilling mud, emulsion stabilizer, food additives, industrial oil adsorbents, insecticide and pesticide carrier, iron ore pelletizing, medicines, nanoclays, organoclays, paint, paper, pencil leads, pharmaceuticals, pillared clays, plasticizers, rubber filler, sealan, slurry trench stabilization, tape joint compounds, water clarification.
Palygorskite-serpentine	Light tan, brown, cream, or bluish green colour Some lattice substitutions Moderate layer charge Medium base exchange capacity High surface area High absorption capacity	Adhesives, agricultural carriers, animal feed binders, anti-cracking agent, barrier sealants, bleaching clays, catalyst support and carrier, ceramics, cosmetics, drilling fluids, environmental adsorbent, industrial floor adsorbents, laundry washing powders, medicines and pharmaceuticals, oil refining, paint, paper, polishes, suspension fertilizer, tape-joint compounds.

The most important factor contributing to the properties of different type of clay minerals is their molecular structure. When one octahedral sheet is linked to one tetrahedral sheet, the clay layer is called 1:1 layer type, such as kaolin subgroup and serpentine subgroup (Madejova, 2003) (Figure 2.1). Within the 1:1 layer type, there are different mineral species, for example, dioctahedral (e.g. kaolinite, dickite, nacrite and halloysite) with a general composition of $Al_2Si_2O_5(OH)_4$ and trioctahedral (e.g. lizardite, antigorite and chrysotile) with an ideal composition of $Mg_3Si_2O_5(OH)_4$ (Madejova, 2003; Brigatti et al., 2006). The composition of the kaolinite, dickite, nacrite and holloysite are characterised by a predominance of Al^{3+} in octahedral sites, although some isomorphous substitution of Mg^{2+}, Fe^{3+}, Ti^{4+}, and V^{3+} for Al^{3+} can occur (Brigatti et al., 2006). However lizaedite, antigorite and chrysolite are trioctahedral layer minerals and they contain mainly Mg^{2+} as central atom in the octahedral sites (Madejova, 2003).

The structure created from two tetrahedral sheets sandwiching on octahedral sheet is called 2:1 layer type, such as smectite subgroup, micas subgroup, pyrophyllite subgroup, vermiculite subgroup and chlorite subgroup (Madejova, 2003; Brigatti et al., 2006) (Figure 2.1). Among these clay mineral subgroups, the most commonly used in various branches of industry is smectite subgroup. This is due to their high specific surface area, high adsorption capacity, chemical and mechanical stability, high cation exchange capacity and swelling ability (Madejova, 2003). The most important species of dioctahedral smectite is montmorillonite, beidellite, nontronite and volkonskoite (Brigatti et al., 2006). Among these species, the most common dioctahedral smectite is montmorillonite where two-third of the octahedral sites are occupied mainly by trivalent cations (e.g Al^{3+}) but partly substituted with (e.g Fe^{3+} and Mg^{2+}). The tetrahedral sites of montmorillonite normally contain Si^{4+} as central atoms with some Al^{3+} substitution

(Madejová et al., 1998). The silica tetrahedra (T) (Si^{4+} in tetrahedral coordination with O^{2-}) and alumina octahedra (O) (Al^{3+} in octahedral coordination with O^{2-}) are interconnected by the sharing of O^{2-} at polyhedral corners and edges in such a way that a sheet of alumina octahedral is sandwiched between two sheets of silica tetrahedral. It is thus referred to as a three-layered clay mineral with T-O-T layers making up the structural unit (Tyagi et al., 2006). Moreover, hectorite, saponite and sauconite represent the trioctahedral species of the smectites. Though Mg^{2+} dominates the octahedral sites in both of these minerals, a partial substitution of Li^{+} for Mg^{2+} occurs in hectorite and saponite which have a pronounced Al^{3+} for Si^{4+} substitution in the tetrahedral sheet (Madejova, 2003). The classifications of clay minerals are presented in Table 2.2.

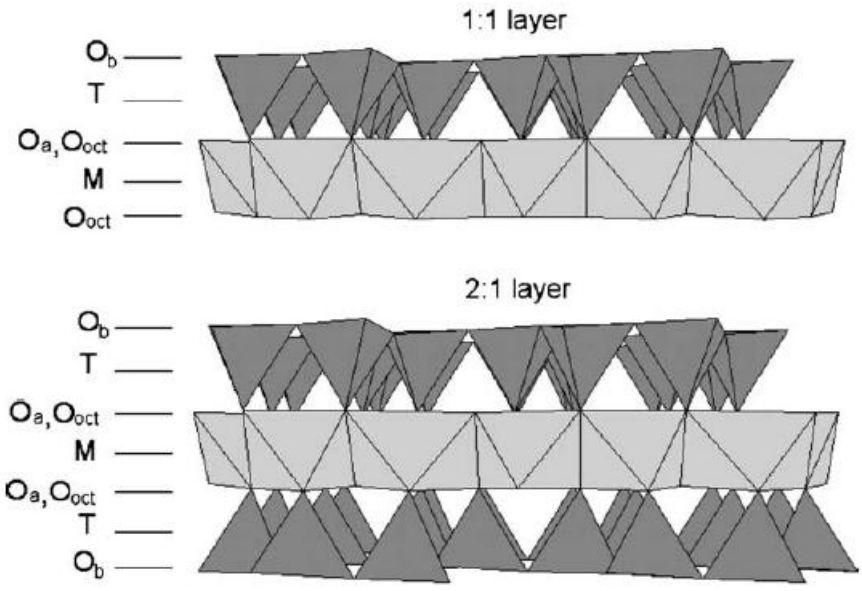


Figure 2.1: The clay mineral structure of 1:1 and 2:1 layer type (adapted from Brigatti et al., 2006)

Table 2.2: Classification scheme of phyllosilicate clay minerals (Adapted from Bailey, 1980)

Layer type	Group (χ = layer charge)	Subgroup	Species
1:1	Kaolin-Serpentine	Kaolinites	Kaolinite, dickite, nacrite, halloysite
	$\chi \sim 0$	Serpentines	Chrysolite, lizardite, amesite
2:1	Smectite or montmorillonite-saponite	Dioctahedral smectites or montmorillonite	Montmorillonite, nontronite, beidellite
	$\chi \sim 0.2$-0.6	Trioctahedral smectites or saponites	Saponite, hectorite, sauconite
	Vermiculite	Dioctahedral vermiculite	Dioctahedral vermiculite
	$\chi \sim 0.6$-0.9	Trioctahedral vermiculite	Trioctahedral vermiculite
	Mica	Dioctahedral vermiculite	Muscovite, paragonite
	$\chi \sim 1$	Trioctahedral vermiculite	Biotite, phlogopite
	Brittle mica	Dioctahedral brittle micas	Marganite
	$\chi \sim 2$	Trioctahedral brittle micas	Seybertite, xanthophyllite, brandisite
2:1:1	Chlorite	Dioctahedral chlorites	
	$\chi \sim 2$	Trioctahedral chlorites	Pennine, dinochlore, prochlorite

2.2 Textural Characteristics

2.2.1 Specific surface area and pore volume

The textural characteristics such as surface area and pore volume play a significant role in the bleaching earth performance (Hassan & El-Shall, 2004). As mentioned earlier, these two factors can be enhanced by modifying the clay minerals with various techniques; including acid, basic, organic, thermal and pillaring treatment (Babaki et al., 2008; Gunawan et al., 2010). According to Murray (1999), the physical and chemical properties of a particular clay mineral are dependent on its structure and composition. For instance, the structure and composition of kaolins, smectites, and palygorskite - sepiolite are very different even though the fundamental building blocks, i.e. the tetrahedral and octahedral sheets, are similar. Smectites and palygorskite–sepiolite are widely used as adsorbent in the purification of vegetable oil. This is due to their fine particle size, high surface area and medium exchange capacity which give smectite, palygorskite and sepiolite a high capacity to absorb and adsorb various liquids, making them very useful in many industrial applications (Murray, 1999). On the other hand, kaolinite exhibits low absorption and adsorption properties, which are directly related to the low surface charge on the particle. They also have a relatively low surface area (8–15 m^2g^{-1}). In addition, the base exchange capacity of kaolinite is typically in the range of 1 to 5 meq/100g (Murray, 2007). As such, no report has been found on examining the possibility of using this clay mineral to bleach the vegetable oil.

Zschau (2001) reported that, natural montmorillonite clay has a specific surface area between 40-160 m^2g^{-1}, whereas the specific surface area of acid-activated is in the range of 150-350 m^2g^{-1}. Valenzuela-Diaz & Souza-Santos (2001), reviewed on the acid activation of brazilian smectitic clays. The authors revealed the works of many researchers to conclude that the specific surface area can be increased greatly with acid

treatment compared to natural clay. The authors also reported that natural smectites have a specific surface area ranging from 16-97 m^2g^{-1} and shows a lower adsorption capacity to absorb colouring matter and other impurities in oils and solutions. In addition to that, the surface area of smectites is several times larger in acid treated clay, reaching values of 200-400 m^2g^{-1}.Compared to untreated clay, acid-activated clay shows a much higher activity (Valenzuela-Diaz & Souza-Santos, 2001). The specific surface area of the raw and activated clay and clay minerals are summarised in Table 2.3.

Table 2.3: The specific surface area of the raw and acid activated clays

Clay minerals	Raw clay S_{BET} (m^2g^{-1})	Acid activated clay S_{BET} (m^2g^{-1})	References
Glauconite	49	326	(Srasra & Trabelsi-Ayedi, 2000)
Bentonite	69	238	(Rozic et al., 2010)
Smectite	63	238	(Novakovic et al., 2008)
Montmorillonite	93	107	(Falaras et al., 1999)
Vermiculite	3.5	275	(Ravichandran & Sivasankar, 1997)
Palygorskite	186	286	(Suarez Barrios et al., 1995)
Glauconite	78	324	(Franus et al., 2004)
Saponite	35	367	(Vicente Rodriguez et al., 1995)
Sepiolite	293	549	(Vicente Rodriguez et al., 1994)
Phlogopite	4	91	(Chmielarz et al., 2010)
Griffithite	35	306	(Vicente et al., 1997
Palygorskite	208	265	(Myriam et al., 1998)

Falaras et al., (1999), investigated the effect of acid activated montmorillonite with sulphuric acid (H_2SO_4) for the bleaching of cottonseed oil. The results revealed that a linear dependence of the bleaching efficiency on the clay surface area and acidity was observed. Moreover, it shows that medium activation of the clay is most effective in bleaching the cottonseed oil. They also stated that the removal of colour and peroxide value appeared higher in the clay sample with the greatest surface area. The largest surface area of acid activated montmorillonite is around 107 m^2g^{-1}. The surface area and pore volume influence the bleaching efficiency of acid activated montmorillonite. They also concluded that enhanced Bronsted surface acidity and surface area are the deciding factors in the bleaching efficiency of acid-activated montmorillonite (Falaras et al., 1999). This effect was also reported by Hassan & El-shall (2004) where large surface area and pore volume play significant roles in the bleaching and adsorption capacity of clay minerals (Hassan & El-shall, 2004).

Working on sunflower oil, Lomić et al., (2004) attempted to correlate the textural properties of raw purified acid activated and Al-pillared samples with its bleaching capacities. The author observed that BET surface area and micropore surface area are not crucial factors for adsorption capacities of clay and clay derivates. They revealed that the bleaching capacity of clay and its derivates are determined by using the sample total pore volume, instead of the sample surface area. This is due to the fact that the adsorbents with higher pore volumes offer the best adsorption capacities. They also suggested that pigments with higher molecules can penetrate only into the pores with higher dimensions, thus micropores do not take part in pigment adsorption during bleaching processes of raw sunflower oil (Lomic et al., 2004).

This effect was also reported by Christidis et al., (1997) where the increase in the surface area is associated with changes in the smectite structure. They stated that, although surface area is an important characteristic of the activated materials, maximum bleaching capacity is not associated with maximum surface area.

This observation was supported by Lin & Yoo (2007), based on their research work, in which they also claimed that the highest removal of iron, phosphorus and secondary oxidation products were not associated with the highest surface area. They stated that although attapulgite clay had lower surface area, 139 m^2g^{-1} and 157 m^2g^{-1}, respectively, they adsorbed more iron, copper, phosphorus and secondary oxidation products than the acid activated bentonite which possessed a higher surface area of 234 m^2g^{-1}.

On the contrary, Srasra & Trabelsi-Ayedi (2000) studied the textural properties of acid activated glauconite in the bleaching of rapeseed oil. Generally, glauconite is a dioctahedral iron illite. The results showed that medium activation of glauconite was most effective in bleaching the rapeseed oil. The best bleaching performance correlates with the maximum of the external specific surface area, but not with the specific surface area and total pore volume. The fairly diverse results may be due to different types of clay used and the different preparation methods of this adsorbent. Noyan et al., (2007) reported the effect of H_2SO_4 activation on the crystallinity, surface area, porosity, surface acidity, and bleaching power of a bentonite. They stated that the bleaching power is controlled more by the pore size distribution rather than other adsorptive properties of the bleaching earth. They concluded that the maximum bleaching power depends more on the mesopore size distribution of the bleaching earth (Noyan et al., 2007).

The adsorption capacity for a specific clay minerals depends on the accessibility of the molecules into pores and consequently on the size of pores of clay minerals (Babaki et al., 2008). According to Gregg & Sing (1982), pore sizes can be classified into three types. The pores of widths below 2 nm are called micropores, those with widths between 2 and 50 nm are called mesopores and those larger than 50 nm are called macropores (Gregg & Sing, 1982). Babaki et al., (2008) reported that, the physical and chemical properties of bentonites such as adsorption and catalytic activity depend extensively on the micro and mesopores. Although the micropores and mesopores are located within the particles, and the macropores are located between the particles, nevertheless the effect of the macropores on the adsorptive properties of a solid is negligible compared to that of the micropores and mesopores. The bentonites clay is the most important among solids that contain natural mesopores and also, contain a small amount of micropores (Babaki et al., 2008).

2.3 Surface Chemistry

In order to identify the adsorbing mechanism of clay minerals, clay surface studies (both outside and interlamellar) have been investigated by Schoonheydt & Johnston (2006), which help to clarify clay's surface, such as adsorbed species' location on the adsorbent and etc. Generally, clay minerals have many attractive features in their structure, namely; active sites such as hydroxyl groups, Lewis and Bronsted acidity, exchangeable interlayer cations and the difference of SiO_4 tetrahedral sheet and $Al_2(OH)_6$ octahedral sheet in chemical stability (Dai & Huang, 1999). Studies of clay mineral's surfaces to date have included active sites and the functional groups. Active sites or surface functional groups are very important, because they determine the chemical reactions. The active site is an atom or a group of atoms that belongs to the solid and can participate in reactions with the species in the surrounding media (Sposito

et al., 1999). When the protonation - deprotonation reactions at the surface of phyllosilicates are considered, the focus is directed to surface oxygens instead of metal ions, because they are the atoms that can become protonated or deprotonated (Schoonheydt & Johnston, 2006).

The reactivity of surface oxygen depends on the type and the spatial distribution of atoms surrounding it; thus a surface functional group is usually written as a single oxygen together with the atoms that are directly attached to it. Therefore, different surface planes exhibit different surface functional groups. They can also be described on the basis of their location (edge or basal surface), geometric arrangement of surface atoms, chemical composition and accessibility (Schoonheydt & Johnston, 2006). Generally, there are six kinds of active sites which are important in explaining the interactions of organic molecules to the clay surfaces. They are isomorphic substitution sites, hydrophobic sites, broken edge sites/hydroxyl surface, neutral siloxane surface, metal cations occupying cation exchange sites and water molecules surrounding the exchangeable cations. Among these active sites, the first four sites are the most important and will be discussed in greater details in this chapter (Schoonheydt & Johnston, 2006).

2.3.1 Isomorphic substitutions

Surfaces of clay mineral particles are classified as having either permanent charge or pH-dependent charge. A permanent charge is derived from isomorphic substitutions in the clay mineral structure and is indifferent to the conditions surrounding the mineral (Matocha, 2006). Isomorphic substitution is the most important active sites on the clay mineral surface which occurs within the tetrahedral and/or octahedral sheets and generates negative charge on the layers (Madejová et al., 1998). Generally, it involves

replacement of constituent metal ions of the lattice by cations of lower charge, generating a net negative charge on the mineral, which is compensated by the positive charge of adsorbed (exchangeable) cations. The substitution can occur during or after crystal formation (Matocha, 2006).

Normally, in 1:1 phyllosilicate minerals, no isomorphic substitution occurs in either sheet, thus kaolinite and serpentine have no significant permanent negative structural charge on basal sites and little cation exchange capacity (Sposito et al., 1999). Isomorphic substitution can create some kinds of active site in the clay lattice of 2:1 layer silicates. This phenomenon happens on the basal surfaces of charged 2:1 layers silicates including smectite, vermiculites and micas. The number of cation positions occupied within the octahedral sheet determines whether a clay mineral is di- or trioctahedral. If Al^{3+} is present in the octahedral sheet, then the mineral is dioctahedral, and trioctahedral if Mg^{2+} is present. Within the smectite group of minerals, dioctahedral montmorillonites have the majority of structural negative charges. These are derived primarily from octahedral site substitutions of Fe^{2+} or Mg^{2+} for Al^{3+} with a structural formula of $Si_8{}^{IV}M_{0.66}H_2OAl_{3.34}{}^{VI}$ $(Fe^{2+}, Mg^{2+})_{0.66}O_{20}(OH)_4$, where M refers to the exchangeable cation balancing the permanent charge produced by substitution of Fe^{2+} or Mg^{2+} for Al^{3+}. The octahedral layer charge for montmorillonite, or the number of moles of excess electron charge per formula unit, would be -0.66, balanced by $M_{0.66}$ exchangeable cations adsorbed near the basal plane of the tetrahedral sheet. In dioctahedral beidellites, tetrahedral substitutions of Al^{3+} for Si^{4+} exceed substitutions in the octahedral sheet. Nontronite is similar to beidellite except it has redox-active Fe^{3+} in octahedral coordination (Figure 2.2) (Matocha, 2006). The vermiculite group differs from the smectite group because the primary source of negative charge arises from a

large degree of Al^{3+} for Si^{4+} substitution in the tetrahedral layer, giving rise to a layer charge greater than that in smectites, ranging from 1.2–1.8 (Matocha, 2006).

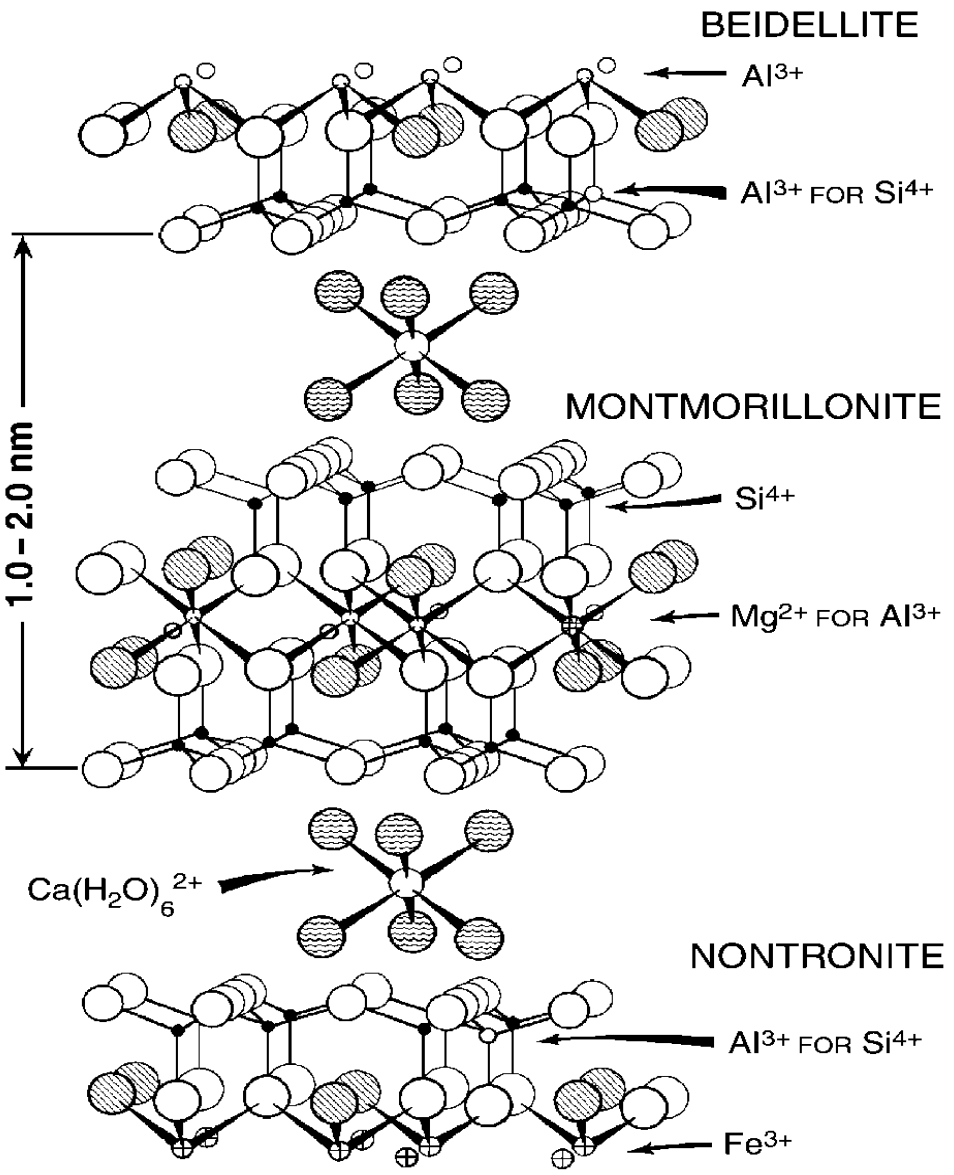


Figure 2.2: Representative of 2:1 phyllosilicate minerals indicating charge sites and different locations of substitutions, (adapted from Matocha, 2006).

Sposito et al., (1999) reported that, when isomorphic substitution occurs in the octahedral sheet, the negative charge is more delocalized and the Lewis base character of the siloxane surface is enhanced. Depending on the extent of isomorphic substitution, these negatively charged sites are separated by distances ranging from 0.7 to 2 nm on

the basal surface. The negative charge that results from isomorphic substitution is balanced by the presence of exchangeable cations which are Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} ions (Sposito et al., 1999). The excess negative charges smear over all the superficial oxygen and make the clay surface highly acidic. Whereas for the sorption of polar and charged organic materials, the location of isomorphic substitution sites in 2:1 layer silicates, for instance on octahedral or on tetrahedral, will have a great impact. Moreover, the extent and type of isomorphic substitution occurring in layered silicates can highly influence the selectivity for inorganic and organic cations, degree of swelling and accessibility of the interlamellar region (Schoonheydt & Johnston, 2006).

2.3.2 Hydrophobicity and Hydrophilicity

Surfaces that attract water are termed hydrophilic, whereas surfaces that repel water are termed hydrophobic. Polar liquids like water and alcohols interact more strongly with hydrophilic surfaces. Similarly, non-polar liquids such as petroleum-based solvents interact more strongly with hydrophobic surfaces. Neutral-layer silicate clays such as talc and pyrophyllite are hydrophobic whereas, clay with an octahedral such as montmorillonite and hectorite and/or tetrahedral such as vermiculite charge deficit is hydrophilic (Jaynes, 2008). Schrader & Yariv (1990) reported that the clay minerals, (e.g. talc and pyrophyllite), are hydrophobic and are not as readily wetted by water as the hydrophilic clay mineral vermiculite. They explained that the hydrophobic and hydrophilic properties of these minerals are based on the electronic properties of the clearage planes. They argued that talc and pyrophyllite are hydrophobic because the oxygen on the cleavage surfaces (siloxane surface) is not good electron donors (Lewis bases) and consequently do not form effective hydrogen bonds to water. In contrast, vermiculite is hydrophilic and they attributed this hydrophilicity to two factors: 1) hydration of exchangeable ions on the clearage faces, and 2) the substitution of Al for Si

in the clearage faces of vermiculite making the oxygen good electron donors (effective Lewis bases) which form hydrogen bonds to water (Sposito, 1984).

Sorption of organic molecules on the clay surfaces can impart a hydrophobic nature to the clay surface (Schoonheydt & Johnston, 2006). Jaynes & Boyd (1991), prepared a series of montmorillonite with reduced-charge and hence, reduced exchangeable cation content. These reduced-charge clays were then exchanged with small organic cations. It can be seen that, the adsorption of aromatic hydrocarbon molecules from water to samples of these reduced-charge organo-clays substantially increased with greater charge reduction and hence, lower organic cation content. Hydrocarbon sorption was found to be proportional to the surface area. This suggests that the hydrocarbons were adsorbed onto the siloxane surface and that this surface is hydrophobic (Jaynes & Boyd, 1991).

2.3.3 Hydroxyl Surfaces

Another type of active sites that clay minerals and related hydroxides possess is hydroxyl surface such as Si-OH and Al-OH or Mg-OH. However, hydroxyl groups located at broken edges, steps and related defects of clay minerals and oxides are different, and are called “terminal OH groups” (Schoonheydt & Johnston, 2006). These OH groups carry either a positive or negative charge depending on the type of metal ion and the pH of the ambient aqueous solution. Hydroxyl groups are strongly dependent on pH value as they became protonated or deprotonated according to the pH value of the solution. At low pH, these sites will develop a positive charge due to the adsorption of protons, so organic acids and oxyanions can interact with these positive charged sites strongly. With the increase of the pH, these sites will develop neutral charge sites and finally will develop a negative charge when taken to very high pH. At the same time,

the role of these edge sites to the cation exchange capacity (CEC) depends on the size and shape of the clay particles. If the particles are large, the CEC from these sites are minimal. On the contrary, if the particles are small, their contribution will become greater. An organic molecule does not replace the exchangeable metal cation, but coordinates directly to the metal cations which occupy the exchangeable cation sites. An organic molecule such as phenol; can interact with exchangeable alkali and alkaline earth metal cations which occupy cation exchange sites (Schoonheydt & Johnston, 2006).

2.3.4 Neutral Siloxane Surface

The neutral siloxane surface is considered to have a predominantly hydrophobic character, which is due to the strong bond formed between the Si and O atoms, hence, the siloxane surface on the clay minerals is the least reactive (Schoonheydt & Johnston, 2006). This surface has interesting sorption properties and is capable of polarizing water molecules surrounding the exchangeable cations. The uncoordinated surface atoms which can donate protons to adjacent organic solutes are also important active sites for clay minerals. The origins of charges on the clay mineral lattice are supposed to be primarily due to the isomorphic substitution, lattice imperfections, broken bonds at the edges of the particles and exposed structural hydroxyls (Schoonheydt & Johnston, 2006).

2.4 Characterisation Methods

There are various experimental techniques being used to characterise the clay minerals such as X-ray fluorescence (XRF), X-ray diffraction (XRD), Cation exchange capacity, Fourier transforms infrared spectroscopy (FTIR), Scanning electron microscope (SEM), Differential thermal analysis (DTA), Thermal gravimetric analysis (TGA), BET surface

area and Pore size distribution (Heller-Kallai, 2006; Tyagi et al., 2006; Meesuk & Vorasith, 2006; Steudel et al., 2009).

The XRF method is widely used to measure the elemental and chemical compositions of materials before and after modification. This method is fast and non-destructive to the sample; therefore, it is the method of choice for bleaching earth applications and industrial production for control of material (Steudel et al., 2009). XRF analysis can be performed on a MagiXPRO spectrometer from Philips equipped with a rhodium X-ray tube (stimulation power: 3.2 KW) using molten pellets. The loss of ignition is determined separately by storing a sample in an oven at 1000 °C for 2 h (Steudel et al., 2009).

XRD is the most widely used technique to identify the crystalline phases present in the clay samples (Temuujin et al., 2004; Habashy et al., 1982; Franus et al., 2004). XRD patterns are obtained on a D8 Advance X-Ray Diffractometer-Bruker AXS with Cu-K_α monochromatized radiation (40 kV and 40 mA). The powder patterns are recorded between 3^o to 70^o 2Θ at a scanning speed of 1^o2Θ/min (Christidis et al., 1997; Rozic et al., 2010).

FTIR spectroscopy is used to analyze the surface chemistry especially different oxides in materials (Madejová, 2003; Tyagi et al., 2006). The equipment can also be used to distinguish between different types of clay minerals and to derive information concerning their structure, composition and structural changes during acid activation. FTIR analysis of the clay samples was conducted on a Perkin-Elmer spectrum 400. The KBr pressed disc technique is used. FTIR spectra is recorded within a range of 400-4000 cm^{-1} at resolution of 4 cm^{-1} (Madejová, 2003).

The surface morphology of the clay samples are analysed by SEM (Hitachi S520 SEM) instrument operating at 20 kV (Christidis et al., 1997).

The BET surface area and pore size distribution are determined from nitrogen adsorption isotherm at 77 K using a Quantachrome Autosorb-1MP instrument. Prior to analysis, the samples are outgassed 24 hours under vacuum at 95^0C. The specific surface areas are determined according to the BET method at the relative pressure in the range of 0.05 to 0.32. The total pore volumes of micro and meso pores are directly determined from the nitrogen adsorption at P/P_O = 0.98. The pore size distribution is calculated using the Barret-Joyner-Haleda (BJH) method using the adsorption isotherm (Temuujin et al., 2004; Rozic et al., 2010).

The cation exchange capacity (CEC) is one of the basic properties of clay minerals. Several methods to determine the CEC have been developed. Mehlich, (1948) determined the CEC by saturating the clay with one cation, then washing out excess salt and finally replacing the cation by several exchange/washing cycles with another cation. The collected solutions were employed for the determination of the amount of replaced cation. Another method involves leaching with ammonium acetate and subsequent replacement of the NH_4^+ ions from exchange sites (Mehlich, 1948; Peech, 1945; Fraser & Russell, 1969; Busenberg & Clemency, 1973). However, this method is time-consuming because the exchange with NH_4^+ ions involves five to six steps. Janek & Lagaly (2003) proposed methods by using cationic surfactants. The advantage of this method is that it can be carried out with simple materials. The preparation of the samples is easy and fast to be carried out. However, the general problem when using surfactants is that an excess will be adsorbed on the clay, requiring determination of the point when the equivalent amount is adsorbed. Lastly, metal-organic complexes are

employed as exchange cations. The affinity of the clay minerals towards this type of cation is high, so that complete exchange can be achieved in one single treatment step (Chhabra et al., 1975). An excess of the complex is added to the clay dispersion and one has only to determine the remaining concentration after the exchange reaction. Cobalthexamine (Ciesielski & Sterckeman, 1997), silverthiourea (Searle, 1986), copper bisethylenediamine (Bergaya & Vayer, 1997) or copper triethylenetetramine (Meier & Kahr, 1999) can be used for this purpose.

Layer charge is an important characteristic of 2:1 layer phyllosilicates (Mermut & Lagaly, 2001) . The layer charge can be determined by the alkylammonium method (Steudel et al., 2009; Lagaly & Mermut, 1994; Lagaly, 1981; Mackenzie, 1951). However, the method is time consuming and requires a number of X-ray diffractograms for one sample. The techniques, such as optical properties of organic dyes can also be used to characterize the layer charge. An alternative way to calculate the charge differences between tetrahedral and octahedral sheets is to determine the cation exchange capacity (CEC) before and after Li fixation (Mackenzie, 1951).

Thermal analysis is a very useful device to characterise clay minerals. The thermal analysis measurements give information on the release of water, phase transformations, decomposition and recrystallisation. Clay minerals contain various kinds of water, which are released at different temperature ranges. First dehydration occurs up to temperatures of around 300°C. During dehydration adsorbed water from the mineral surfaces and interlayer water from inner surfaces are released in endothermic reactions. The dynamic mass loss during the dehydration is equal to the static determined water content at 200°C. Dehydroxylation occurs between 330°C and 850°C. During dehydroxylation structural water associated with hydroxyl groups migrates out of the mineral structure. The dehydroxylation temperature gives information about the

stability of clay minerals and is associated with the structure of the octahedral layer of dioctahedral 2:1 clay minerals. Thermal analysis is a combination of thermogravimetry (TG) with differential thermal analysis (DTA) or differential scanning calorimetry (DSC). The samples were measured at a defined temperature-time-program with a defined heating rate (Steudel et al., 2009).

2.5 Activation Techniques

Activation is defined as a chemical or physical treatment applied to certain types of clays to develop a capacity to absorb colouring matter and other impurities in oils and solution (Valenzuela-Diaz & Souza-Santos, 2001; Babaki et al., 2008). Physical and chemical behaviors of clay minerals are studied by numerous researchers because of their relation to their adsorbing and catalytic properties. The behavior is governed by the extent and nature of their external surface which can be modified by suitable treatments (Rodriguez et al., 1994). The treatments or modification of clay minerals can be categorised into 1) physical modification (thermal or microwave treatment) which involves alteration of chemical composition and crystalline structure by the effect of high temperature, 2) chemical modification is usually alteration of structure and surface functional groups and 3) pillaring treatment which involves chemical and physical restricting of the clay mineral structure to increase capacity for adsorption or to create spaces that encourage adsorption of specific ions (Figure 2.3).

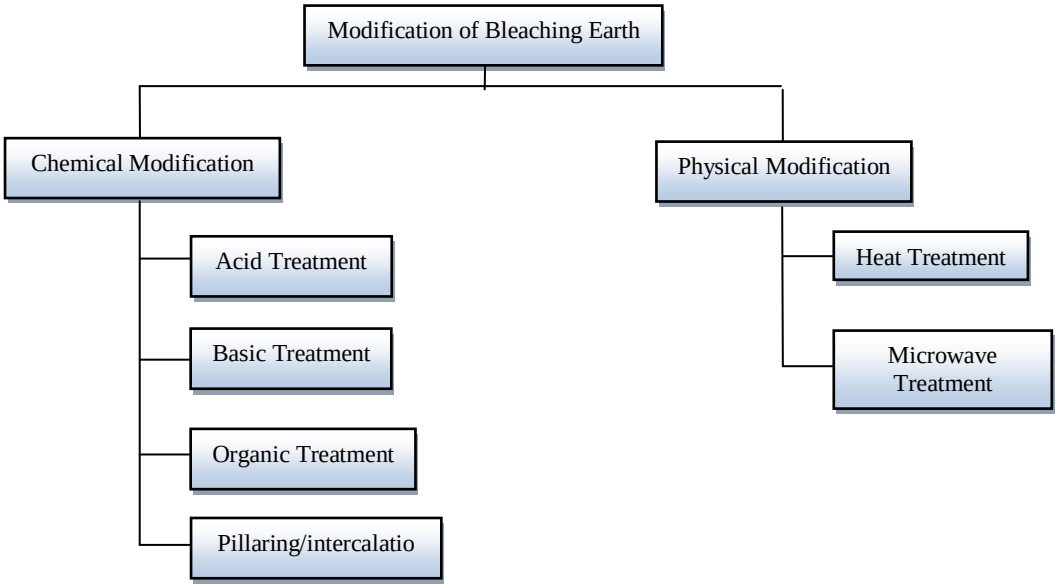


Figure 2.3: Categories of bleaching earth modification techniques.

2.6 Modification of chemical characteristics

2.6.1 Acid treatment

Acid treatment is one of the most common chemical modifications of bleaching earth (Komadel & Madejova, 2006). In general, acid activation process consists of two steps; 1) the substitution of the exchangeable cations by protons and 2) the dissolution of metal ions from the clay structure, by depopulating the octahedral sheet (Figure 2.4) (Fernandes et al., 2007; Kaviratna & Pinnavaia, 1994).

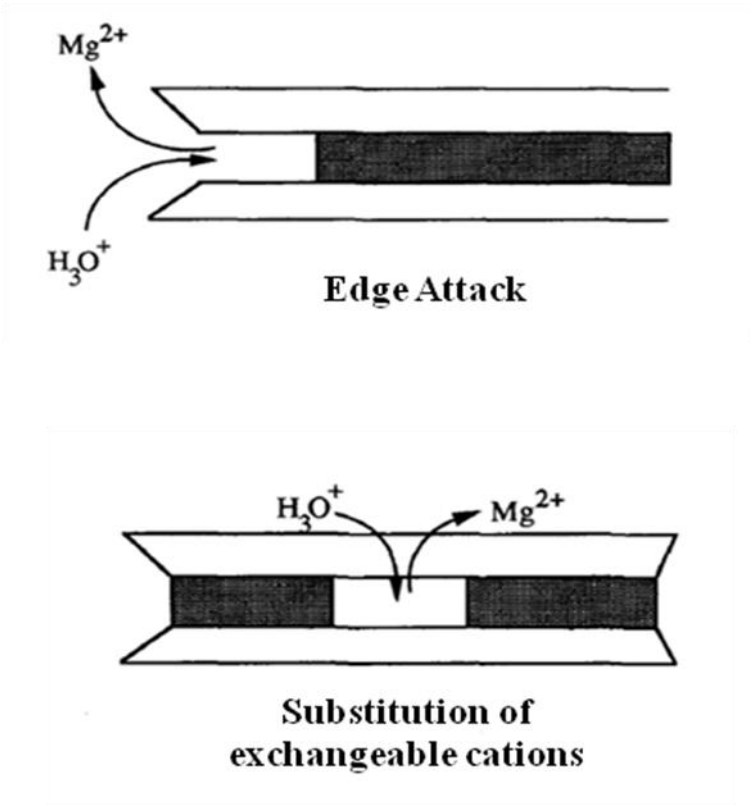


Figure 2.4: Mechanism of the effect of acid activation (Kaviratna & Pinnavaia, 1994)

A similar description was made by Madejová et al., (1998) where during the acid attack the interlayer cations are replaced by protons and the octahedral cations (Al^{3+},Mg^{2+}, Fe^{2+}, Fe^{3+}) are dissolved. The products are X-ray amorphous, of high SiO_2 content, and show a high specific surface area and micro and mesopores. The bleaching power depends on the activation procedures (acid concentration, temperature and time). The composition of the clay minerals layers significantly affects their stability against the acid attack, with trioctahedral layers dissolving much faster than dioctahedral layers. An increase in Mg and/or Fe for Al substitution in dioctahedral smectites would increase their dissolution rate in acids (Madejová et al., 1998; Breen et al., 1995). As reported by Agnello (2005) in further treatment, the acid penetrates accordingly from the crystal surface deeper and deeper into the crystal structure of the individual layers, which causes the inner surface of these crystal platelets to increase in size and active acid centers to be formed (Agnello, 2005).

As a result acid activation promotes catalytic activity by increasing the number of Bronsted and potential Lewis acid sites (Chitnis & Sharma, 1997). Srasra & Trabelsi-Ayebi (2000) studied the effect of bleaching treatment on the textural properties of acid activated glauconite. The results show that, the colour pigment and impurities in the bleaching process can be eliminated by acid treatment. They found out that adsorption of carotenoid can be catalysed by the Bronsted and Lewis acidity as shown in Figure 2.5. β-carotene attaches to the clay surface in the form of carbonium ions either by forming coordination bonds with Lewis sites or by forming hydrogen bonds with Bronsted sites of the activated clay mineral (Sarier & Güler, 1989). The acid treatment has been used to increase the specific surface area, modify the surface functional group, to obtain solids with high porosity and to increase the number of acidic centers. The most important role is to enhance the adsorption capacity for the removal impurities and colour pigment from the oil. Figure 2.6 is a simplified flow diagram of the process in the production of acid activated bleaching earths.

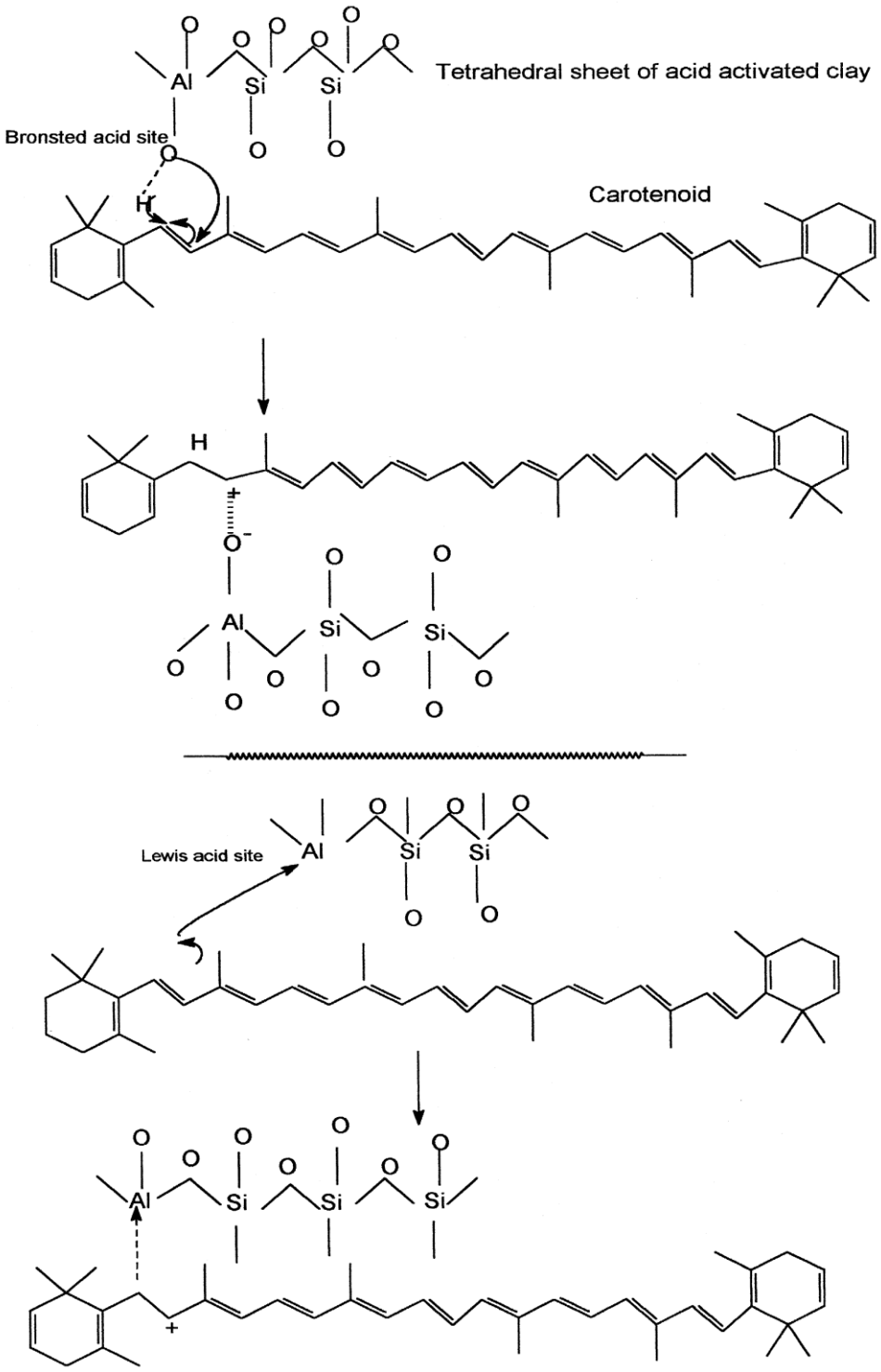


Figure 2.5: The mechanism of carotenoid adsorption on Bronsted and Lewis acid sites (Srasra & Trabelsi-Ayedi, 2000)

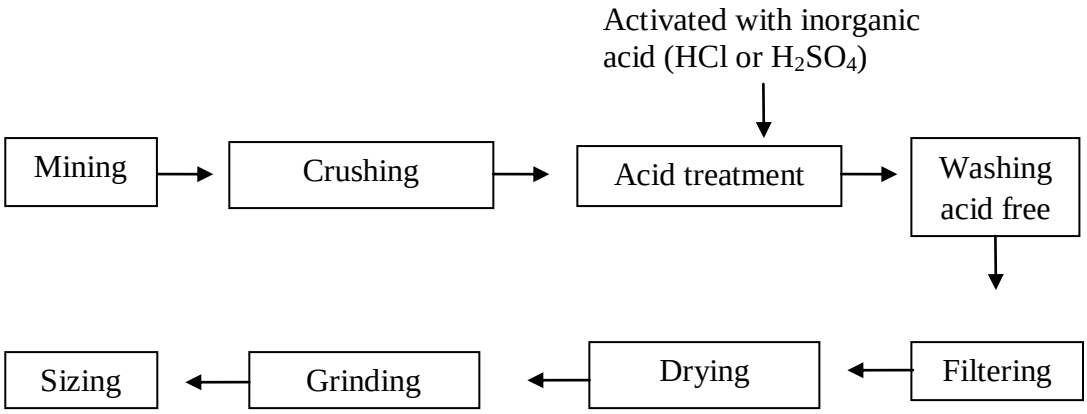


Figure 2.6 Simplified flow diagram of the process of acid activated bleaching earth (Richardson, 1978)

Numerous studies have been reported on the acid treatment of clays, especially on bentonite-smectite or montmorillonite (Foletto et al., 2006; Wu & Li, 2009; Okwara & Osoka, 2006; Falaras et al., 1999; Tyagi et al., 2006; Christidis et al., 1997; Sarier & Guler, 1989; Kashani Motlagh et al., 2008; Didi et al., 2009; Allo & Murray, 2004; James et al., 2008; Novakovic et al., 2008; Rozic et al., 2008; Konta, 1995; Li et al., 2003; Howard & Roy, 1985; Gates et al., 2002; Novak & Cicel, 1978; Oboh & Aworh, 1988; Juanmao et al., 2008; Onal & Sarikaya, 2007; Onal, 2007); saponite (Vicente Rodriguez et al. 1995; Vicente et al., 1997); vermiculite (Ravichandran & Sivasankar, 1997; Chmielarz, 2010); kaolin (Gonzalez & Ruiz, 2006; Hosseini, 2007; Mahmoud & Saleh, 1999); palygorskite-sepiolite (Chitnis & Sharma, 1997; Suarez Barrios et al., 1995; Vicente Rodriguez et al., 1994; Myriam et al., 1998) and glauconite (Hassan & El-Shall, 2004; Srasra & Trabelsi-Ayedi, 2000; Franus et al., 2004). Among all of these, bentonite is the most commonly used for the production of acid-activated clays in the purification of vegetable oils (Didi et al., 2009; Christidis, 1998; Hisarli, 2005; Eloussaief et al., 2009). Bentonite has always had a wide range of markets and acid-activated bentonite has been a traditional product for many decades. It is usually a Ca-bentonite that is treated with organic or inorganic acid solutions to replace divalent

calcium ions with monovalent hydrogen ions and to leach out ferric, ferrous, aluminium and magnesium ions, thus, altering the layers of smectite and increasing the specific surface area and porosity (Komadel & Madejova, 2006).

There are various types of acids used for acid treatment including inorganic acid such as Hydrochloric, Sulphuric and Nitric and organic acid such as Acetic, Citric, Oxalic and Lactic. Among all of these, Hydrochloric acid (HCl) and Sulphuric acid (H_2SO_4) are probably the most widely used in acid activation, because they show strong effects as affected by the processes parameters and good results in specific surface area, porosity and adsorption capacity (Valenzuela-Diaz & Souza-Santos, 2001; Siddiqui, 1968).

2.6.1.1 Inorganic acids

Komadel et al., (1996) have investigated the effect of acid type and concentration on the reaction rate and products of dissolution of hectorite in inorganic acids. The authors reported that the rate of hectorite dissolution decreased in the order $HCl \geq HNO_3 > H_2SO_4$ at the same molar concentration. The dissolution rates of Li^+ is distinctly greater than that of Mg^{2+} in all acids at low acid concentrations. The results indicated that at lesser acid concentrations, protons are attacked preferentially to the Li^+ (in the octahedral sheet), where the local negative charges are located. However, when the acid concentration is increased, the respective dissolution rates for Li^+ and Mg^{2+} in any given acid apparently converged to a similar value (Komadel et al., 1996). Van Rompaey et al., (2002), reported that the dissolution rates of Li+ were slightly greater than that of Mg^{2+}. The results were similar with the conclusion made by Komadel et al., (1996). On the contrary, Van Rompaey et al., (2002) concluded that the sequence for the dissolution rate of hectorite decreased in the order $H_2SO_4 \geq HNO_3 > HCl$ for equal molar concentration. The order of dissolution is different with that found by Komadel et

al., (1996). The differences in the results are clearly demonstrated by the dissolved fractions. For example; at 1 M H_2SO_4 for 8 h, more than 70% of all Li+ dissolved, whereas at the same molar concentrations, HNO_3 and HCl dissolved at 58% and 53%, respectively (Van Rompaey et al., 2002).

Hongping et al., (2002), reported that when Ca-montmorillonite samples are activated by H_2SO_4, there is progressive dissolution of the octahedral layers. The order of dissolved cations in the octahedral sheet of montmorillonites observed is MgO > Fe_2O_3 > Al_2O_3. The content of Al_2O_3 decreases significantly due to the dissolution of octahedral Al, whereas the proportion of SiO_2 increases relatively (Hongping et al., 2002). This effect was also reported by Suarez Barrios et al., (1995), where with increasing acid concentration, the content of SiO_2 increases and the content of octahedral cations Al_2O_3, MgO and Fe_2O_3 decreases. Treatment of palygorskite with mineral acid resulted in an increase in the percentage of SiO_2 and a decrease in Al_2O_3, MgO and Fe_2O_3 which are related to the progressive dissolution of palygorskite. The BET surface area of the original palygorskite increases from 186 m^2g^{-1} to 286 m^2g^{-1}, after which it decreases. The reasons for the increase are mainly due to the elimination of exchangeable cations and generation of silica (Suarez Barrios et al., 1995). A significant increase in the specific surface area was also observed by the treatment of clay with mineral acids (Komadel & Madejova, 2006). It has also been observed by several other researchers, for instance: Vicente Rodriguez et al., (1994); Salem & Karimi, (2009); Suresh et al., (2007); Mills et al., (1950) and Myriam et al., (1998). On the other hand, in the treatment of clay with mineral acids at high acid concentration (e.g. 7 N HCl) the structure of the palygorskite was completely destroyed (Suarez Barrios et al., 1995). Consequently the BET surface area of the clay is diminished, which in turn diminished the decolourizing power (Al-Zahrani, 1995). Their work does

not contradict with that of Franus et al., (2004) which has stated that the layer structure of the glauconite is preserved with mineral acid.

Taylor & Ungermann (1991), patented the procedures for making acid activated bleaching earth using high susceptibility source clay and novel bleaching earth product. The process involves treating mixtures of palygorskite clay (attapulgite or sepiolite) and bentonite with H_2SO_4 in the amount corresponding to an acid dosage in the range of 1 to 10% by weight. The results indicated that several advantages can be achieved from the invention including lower acid costs/unit mass of clay treated, lower production costs (does not involve washing, filtering or waste treatment process) and environmental friendly (no harmful environmental waste products are produced).

Steudel et al., (2009), studied on the dissolution behavior of six bentonites with a high content of dioctahedral smectites, a hectorite and vermiculite. They used two types of inorganic acid such as HCl and H_2SO_4 at the same molar concentration. The results reveal that the dissolution of the octahedral cations like Al, Mg and Fe are most effective with 10 N H_2SO_4 compared to any concentration of HCl. Most of the octahedral cations were dissolved by the treatment with 10 N H_2SO_4. At the same molarity, the reactivity of HCl is weaker than H_2SO_4 due to the lower concentration of protons. Similarly, behaviors against both acids were observed in vermiculite and hectorite samples. They are much more stable against acid attack than dioctahedral smectites, and their stabilities are affected by the content of Fe and Mg in the octahedral sheet (Steudel et al., 2009).

A research by Salawudeen et al., (2007), shows that acid treatment increases the bleaching capacity to remove colour from oil up to 94.28% in HCl activated clay and

89.46% bleaching capacity was achieved with H_2SO_4 activated clay. The results indicated that the use of HCl activated clays is proven to be more effective for the removal of colour from oil than H_2SO_4 (Salawudeen et al., 2007). Al-Zahrani, (1995) compared the activation of the clay by inorganic acid and calcination for corn oil bleaching. The results reveal that the highest percentage of bleaching for natural clay activation using H_2SO_4 at compositions of 25%, 35% and 55% by weight, was obtained at 33%, 38% and 40%, respectively. The maximum of percentages of bleaching for natural clay activation in HCl at compositions of 4% and 10% by weight, are 33% and 43%. The author concluded that HCl is more effective in the activation of the local clay than H_2SO_4. On the other hand, acid activation of the clay after calcination using 35% H_2SO_4 gave better results in the percentage of bleaching up to 83% and it shows that H_2SO_4 is more effective in activation of the local clay after calcination than HCl (Al-Zahrani, 1995).

Sabah & Majdan, (2009) chemically modified a sepiolite by mixing it with HNO_3 in order to investigate the adsorption of phosphorus (P) from rapeseed oil. The initial concentration of P in the oil is 29.7 mg/kg. The adsorption capacity of P per unit weight of acid-activated sepiolite (AAS) decreased from 2.50 to 1.84 mg/kg at 80^{o}C and from 2.98 to 1.91 mg/kg at 100^{o}C, corresponding to 0.5–1.5% AAS dosages, respectively. It is evident that there is a decrease in the adsorption of P with AAS dosage for both temperatures, which results from the fact that the adsorption sites remain unsaturated during the bleaching process. At low AAS/oil ratios, the removal of phosphorus observed was more efficient, this is due to the fact that most active adsorption centers are occupied by phosphorus, whereas at higher AAS/oil ratios, competition between phosphorus and colour bodies in the adsorption process occurs (Sabah & Majdan, 2009). A similar observation was made by Sabah (2007), where he reported that

sepiolite treated with 1 N HNO_3 is a superior adsorbent for the removal of chlorophyll-*a* under the optimum conditions of 100^{o}C bleaching temperature and 1.5% sepiolite dosage respectively. Under this condition, chlorophyll-*a* level in the rapeseed oil was reduced from 4.85 to 0.16 mg/kg (Sabah, 2007).

2.6.1.2 Organic acids

Treatment of clay with mineral acids such as H_2SO_4 or HCl may generate new surface acid sites quickly, but they may also cause extensive leaching of $A1_2O_3$ from the clay mineral, thereby leading to structure collapse (Mokaya & Jones, 1995; Mahmoud & Saleh, 1999; Suarez Barrios et al., 1995). In contrast, organic acids may preserve the clay structure, but are less effective in generating surface acid sites (Mahmoud & Saleh, 1999). Moreover, organic acids dissolve less of Al_2O_3 and thus its activation power is much lesser than mineral acids (Al-Zahrani, 1995). The influence of inorganic and organic acid on the de-tert-butylation activity of Jordanian bentonite and kaolin were studied by Mahmoud & Saleh (1999). The results indicated that 1 N HCl is the best acid solution for the activation of bentonite and kaolin samples; after 0.5 h of reaction, 90% and 92% conversions were obtained for both samples, respectively. This is due to the fact that HCl is a strong acid, which completely dissociates in water to H^+ and Cl^- ions. Also, the metal chlorides produced as a result of this acid treatment are completely soluble in water, and removed by the pretreatment process. On the other hand, acetic acid is a weak acid and hence is far less effective for activation of the clays compared to HCl of the same concentration. A conversion of 66% after 0.5 h reaction was observed for both samples when treated with 1 N acetic acid. Moreover, phosphoric acid was more effective than acetic acid and was comparable to HCl. This may be attributed to phosphoric acid being stronger than acetic acid, but is still weaker than HCl (Mahmoud & Saleh, 1999).

Sutheimer et al., (1999), compared the surface characteristics and dissolution behavior of well crystallized (KGa-1b) and poorly crystallized kaolinite (KGa-2). The dissolution experiments were conducted in oxalic acid and inorganic acids at pH 3 at 22°C. Dissolution rates in 1 mM oxalic acid were approximately twice as fast for KGa-2 as for KGa-1b, while it is similar in HNO_3. The comparable dissolution rates for these two sedimentary kaolinites suggest that the fundamental structure of kaolinite has a greater influence on the dissolution kinetics rather than specific surface details. For dissolution in 1 mM oxalate, Al-oxalates complexes were observed almost exclusively in agreement with results of equilibrium speciation calculations. For dissolution in HNO_3, uncomplexed Al species were identified. It can be seen that, Si release is similar for inorganic vs. organic acids for KGa-1b. However, Si release is substantially greater in organic than inorganic solution for KGa-2 (Sutheimer et al., 1999).

In a separate study, Samsuri & Irawan (2004) investigated the removal of iron from Sabah montmorillonite by extracting with three organic acids (citric, gluconic and oxalic acid). They believe that, the bleaching earth also can be treated with organic acid. Among all the organic acids, only oxalic acid is suitable for use on a large scale. It is capable of removing the iron oxides from montmorillonite, but extraction is effective only in a strong acid medium ($pH \leq 2$), at this condition, oxalic acid dissolves a great quantity of iron, forming a soluble complex (Samsuri & Irawan, 2004).

Oboh & Aworh (1988), demonstrated the use of organic and inorganic acid for palm oil bleaching. They used hydrochloric, sulphuric and acetic acid at different molar concentration. The results indicated that bleaching power of clays treated with HCl and H_2SO_4 increased with the concentration of acid to a maximum and declined thereafter. In contrast, clays treated with acetic acid demonstrated lower bleaching power which is

equivalent to 45.59%, when the concentration of acid was at a maximum. Clays treated with HCl and H_2SO_4 are more effective in bleaching the palm oil than those treated with acetic acid (Oboh & Aworh, 1988).

However, the criteria for choice, either organic or inorganic acid in the industrial process, depends on the nature and type of clay, concentration of the acid, temperature and the time of treatment during acid activation (Valenzuela-Diaz & Souza-Santos, 2001). Several other acid treatment experiments under different operating conditions have been reported in literatures in particular the choice of acid used, types of clay, temperature, concentration of acid, and activation time (Foletto et al., 2006). Table 2.4 and 2.5 summarise the advantages and disadvantages of inorganic and organic acid in acid activation.

Table 2.4: Summary of advantages and disadvantages of inorganic acid in acid activation

Type of Acid	Advantages	Disadvantages	References
Inorganic acid	Increases BET surface area and pore volume		Suarez Barrios et al., 1995
Inorganic acid	Fastest in dissolution of octahedral cation such as Fe, Mg and Al		Suarez Barrios et al., 1995
Inorganic acid	More effective in bleaching the palm oil		Oboh & Aworh, 1988
Inorganic acid	May generate new surface acid sites quickly		Mahmoud & Saleh, 1999
Inorganic acid		May destroy the clay structure	Al-Zahrani, 1995
Inorganic acid	Removes high content of free fatty acid, peroxide value and phosphorus		Falaras et al., 1999

Table 2.5: Summary of advantages and disadvantages of organic acid in acid activation

Type of Acid	Advantages	Disadvantages	References
Organic acid	Preserves the clay structure		Mahmoud & Saleh, 1999
Organic acid	Dissolves a great quantity of iron		Samsuri & Irawan, 2004
Organic acid		May decrease BET surface area and pore volume	Al-Zahrani, 1995
Organic acid		Less effective in generating surface acid sites	Mahmoud & Saleh, 1999
Organic acid		Dissolves less of Al_2O_3	Al-Zahrani, 1995
Organic acid	Removes high content of free fatty acid, peroxide value and phosphorus		Habashy et al., 1982
Organic acid		Lower bleaching power and less effective in bleaching palm oil	Oboh & Aworh, 1988

2.6.2 Basic treatment

There were several studies carried out to determine the effects of basic treatment of bleaching earth on the adsorption capacity. In a research article by Novikova & Korsakov, (2003) after treating the clay with 0.5 N Sodium Hydroxide (NaOH) solution, the content of the active centers lowered, and the surface acidity decreased from 1.2 to 0.33. The specific surface area also decreased from 19.3 m^2g^{-1} to 15.2 m^2g^{-1} after the base treatment at 20^oC. At the same time, the content of the sorption centers decreased, although it was slightly greater after treatment at 105^oC. This is probably due to the precipitation of amorphous and finely crystalline silicates and aluminosilicates.

After the treatment with NaOH solution at 20^{o}C, the total content of the active centers increased from 0.19 to 0.31 mg-mol/100g. After further treatment with 5.0 N NaOH solution, the content of the Lewis acid and base centers increased, and the content of the Bronsted centers decreased. The specific surface area after the base treatment at 105^{o}C substantially decreased to 10.5 m^2/g. It was found that the use of base treatment shows a lower adsorption capacity to absorb colouring matter and other impurities in oils and solutions (Valenzuela-Diaz & Souza-Santos, 2001; Novikova & Korsakov, 2003).

Okwara & Osoka, (2006) studied the influence of caustic activation of local clays for palm oil bleaching. Their findings indicated that the adsorption capacity for bleaching earth increased up to 79% at the optimum concentration of 1.0 N NaOH. Compared to the base treatment, acid treatment shows a much higher adsorption activity which increases up to 99%. Although there are a few studies for the base activation effect on the adsorption capacity of bleaching earth, they believe that base activation is also suitable for use in palm oil bleaching. This is because the cost of sodium hydroxide (NaOH) is much lesser than that of inorganic acid such as H_2SO_4 and HCl (Okwara & Osoka, 2006).

2.6.3 Organic treatment

According to Gunawan et al., (2010) the use of acid-activated bentonite for the purification of palm oil has led to several problems such as corrosion of the process vessels, increasing of free fatty acids (FFA) and peroxide value (PV) in oil products and can cause environmental problems. Therefore, in order to reduce these problems, bentonite was modified with cationic and anionic surfactants for the removal of colour pigment, free fatty acids and peroxide value from bleaching palm oil. They used cetyl trimethylammonium bromide (CTAB) and linear alkylbenzene sulfonate (LAS) as

surfactant and the process was conducted under conventional heating and microwave irradiation technique. The results showed that, the highest colour removal was observed with LAS under microwave irradiation technique. It is indicated that LAS is more effective as a bleaching agent than CTAB (Gunawan et al., 2010).

2.6.4 Intercalation/Pillaring

Pillaring is a type of modification method which alters the properties of bleaching earth by using combination of chemical and physical treatment. Pillaring is defined as a process by which a layered compound is transformed in a thermally stable micro- and/or mesoporous material with retention of the layer structure (Fernandes et al., 2007; Mahmoud & Saleh, 1999; Ferraris, 2006; Caglayan et al., 2005). Pillared clay minerals have attracted increasing attention, particularly from the industry since the 1970s, because of their microporous nature and catalytic potential. However, pillared clay minerals have not been used as commercial adsorbents and catalysts. This is because the treatment is the laboratory oriented and it is difficult to extend to an industrial scale (Bergaya et al., 2006).

Generally, the pillaring treatment is presented as a way of increasing the accessibility of the clay layers, but an alternative viewpoint is that it stabilizes ‘oxide’ particles of nanometer dimension that prevent aggregation by interaction with the layers. Thus, the surface groups exposed by these ultra-dispersed ‘oxides’ probably play a key role in determining the promising adsorptive and catalytic properties of pillared clays (Bhattacharyya & Gupta, 2008). The clays pillared with metal oxides are of great importance because of their high thermal stability, high specific surface area, and high catalytic activity. These materials are normally prepared by ion-exchanging cations in the interlayer region of swelling clays with bulky alkylammonium ions, polynuclear

complex ions bearing inorganic ligands (hydroxo ligand or chloro ligand) and large metal complex ions bearing organic ligands. The intercalated inorganic species are capable of preventing the collapse of the interlayer spaces, propping open the layers as pillars, and forming interlayer space. At high temperature, the intercalated inorganic species are converted to metal oxide clusters, generating a stable microporous structure with a high surface area (Bhattacharyya & Gupta, 2008). Pillared clays having large surface areas with high catalytic activity have been reported by numerous researchers and these higher surface area (>200 m^2/g) clays could be intended for use in bleaching vegetable oils. Due to their enhanced acidity and high surface area, pillared clays are extensively used as adsorbents, catalysts, catalytic supports, membranes and bleaching media (Bhattacharyya & Gupta, 2008).

Falaras et al., (2000), investigated the physical and chemical properties of the pillared materials in order to determine the effect on the capacity for adsorbing coloured species from vegetable oils and the bleaching efficiency in the processing of Greek cottonseed oil. They reported that, the bleaching efficiency of the final pillared product depends on the level of the acid activation. The results show that, the pillared materials have high bleaching efficiencies, comparable to that obtained with a commercial industrial bleaching earth (Tonsil) and more than twice that of the untreated clay (Falaras et al., 2000). Davies et al., (1996) in his patent (US 5486499) described the procedures for making pillared clay as effective adsorbents for use in the purification of vegetable oils and found that pillared clay shows the highest bleaching capacity to remove chlorophyll from the oils at 70% and even up to about 99% in some instances.

In an article by Bergaya et al., (2006) numerous studies have been reported on the history, synthesis, properties and applications of the pillared clays. However, there are a

few studies on new method and effective process of pillared clay. Bergaya et al., (2006) suggested that, to be of useful interest, these pillared clays must be used in some industrial or environmental applications and researchers have to pay more attention to the fundamental point of view towards the pillaring processing methods.

2.7 Modification of physical characteristics

2.7.1 Heat Treatment

Apart from chemical modification, the physical modifications using thermal treatment also plays an important role for bleaching earth. The most common physical modification is thermal treatment. The structure and composition of clay minerals can be modified by heating at high temperature (Heller-Kallai, 2006). Some physicochemical properties of bentonites such as swelling, strength, cation exchange capacity, particle size, specific surface area, surface acidity and catalytic activity as well as mineralogy can change considerably depending on the thermal treatment (Onal & Sarikaya, 2007; Sarikaya et al., 2000). Many studies have been reported on the adsorptive and catalytic properties of acid activation of clays (Nguetnkam et al., 2008; Joy et al., 2007; Sabah, 2007; Kheok & Lim, 1982; Falaras et al., 2000; Sabah & Celik, 2005). However, there are only few studies for the thermal effect on these properties (Sarikaya et al., 2000; Alemdaroğlu et al., 2003).

In a research article by Sarikaya et al., (2000) the results of the thermal analysis, show that dehydration is a physical event where water is lost without structural loss, whereas the dehydroxylation is a chemical event that invokes decomposition. As the temperature increases to 400^{o}C, cation exchange capacity decreases slightly because of reversible dehydration. As the temperature increases above 500^{o}C, the space between the crystal layers is reduced and swelling decreases gradually because of irreversible dehydration

and dehydroxylation (Sarikaya et al., 2000). It was shown by Ŏnal, (2007) that the crystallinity and porosity of smectites found in bentonites as major clay minerals were greatly reduced by the thermal treatment. The results reveal that the change by dehydration up to 400^{o}C is reversible. Such properties after heating above 600^{o}C reduced irreversibly. Moreover the crystal structure of the smectite collapsed irreversibly at 900^{o}C. The specific micropore volume increased rapidly to a maximum of 0.045 cm^3 g^{-1} while the heating temperature rises to 400^{o}C by the effect of dehydration and then decreased rapidly by the effect of dehydroxylation and reached zero at 900^{o}C by the effect of decrystallization. The maximum of the specific mesopore volume was attained at 400^{o}C, with the values of 0.115 cm^3 g^{-1}. The specific mesopore volume did not change considerably up to 800^{o}C and then decreased rapidly while the temperature increased from 900^{o}C to 1300^{o}C. This is due to the collapsing of the crystal structure of the smectite and interparticle sintering. The specific surface area of smectite increased to its maximum of 90 m^2g^{-1} at 400^{o}C, after which is decreased to zero at 1300^{o}C (Onal, 2007).

Mathers et al., (1955), investigated the effect of acid and heat treatment on montmorillonoids. The results show that heating H- and Al-montmorillonites at 100^{o}C and 200^{o}C for 12 h, caused considerable reduction in the amounts of exchange acidity, but did not reduce water sorption. In contrast, the Li-montmorillonite suffered almost complete loss of cation exchange capacity and became non-expanding on heating to 200^{o}C. Heating at 300^{o}C for 12 h caused large loss in cation exchange capacity and produced irrevisible dehydration of both H- and Al-montmorillonites. This was proven by the water sorption and the 001 spacing. The H- and Al-nontronite, however, remained expanding and retained its lattice charge at 300^{o}C. At 400^{o}C, lattice hydroxyls had been expelled from the nontronite, though some regularities in the C-direction

persisted. In addition, montmorillonites with largely octahedral charge had smaller cation exchange capacity after heating to 500^{o}C than did montmorillonites with appreciable tetrahedral charge (Mathers et al., 1955).

Ilic et al., (2010), stated that the main changes revealed by heat treatment were initially observed at temperatures below 200°C where the release of water absorbed in pores and on the surfaces occurs. Between 200°C and 450°C, mass loss attributed to the pre-dehydration process takes place, as a result of the reorganization in the octahedral layer. In the temperature range of 450–650°C, dehydroxylation of kaolinite and formation of metakaolinite takes place, while at about 1000°C, mullite was formed, as indicated by an exothermic peak. The observed endothermic peak with a maximum at 552^{o}C may be attributed to dehydroxylation process. The results show that at calcination temperatures of 550°C, 600°C and 650°C, mass loss increased up to 2 h, while prolonged heating has a negligible effect on the mass loss. For all applied heating times at temperature 700°C, the obtained values for mass loss are nearly the same ~ 12%. It can be seen that at calcination temperature of 650°C and heating time of 2 h, mass loss is almost identical with the values obtained at 700°C. Therefore, the optimal parameters for calcination are temperature of 650°C and heating time of 2 h (Ilic et al., 2010).

As reported by Štubňa et al., (2006), dehydroxylation begins at the temperature of 420°C. When kaolinite is heated beyond the limit of the temperature of the dehydroxylation endotherm, a new phase called metakaolinite is formed. During this reaction, as XRD shows, the higher-order reflections lost their intensity and vanished in the XRD background. This result led to the opinion, that the matakaolinite can be amorphous, now a conception of the short-range order crystalline structure of metakaolinite predominates. The loss of high-order reflections indicates that

dehydroxylation results in structural disturbances through the breaking of unstable bonds. As a result, the degree of ordering becomes lower than that in kaolinite as dehydroxylation progressed. The metakaolinite does not collapse but, rather, retains a layered structure. In addition, this has resulted in a decrease in the specific mass of the kaolinite from 2.64 gcm^{-3} to 2.51 gcm^{-3}, increased the porosity of kaolin from 45% to 50% as well as increased its specific surface area to 5 m^2g^{-1} (Štubňa et al., 2006). A similar observation was made by Varga, (2007) where the results of isothermal firing shows that the dehydroxylation begins at 420°C. During dehydroxylation process, octahedral layer is likely to be changed more than the tetrahedral silica layer.

Habashy & Gadalla, (1982) reported that increasing the heat treatment temperature from 110-150^oC invariably involves a marked increase in the specific surface area and total pore volume of the treated clays. In addition, with further increase in the temperature of treatment to 250^oC, although the percentage loss still increases because of the increased loss of the water content, it leads to the decrease in the specific surface area and the total pore volume of the Maadi clay C (M). Similarly to the Alexandria-Cairo road clay C (A), by increasing the heat temperature, the specific surface area and total pore volume obtained also increased, after which it decreased (Habashy & Gadalla, 1982). Al-Zahrani, (1995) compared the bleaching power of clay samples by calcination and without prior calcination. The results indicated that the maximum bleaching power of the local clay activated by calcination or by acid treatment alone is low and rarely exceeds 50%. However, acid activation of the clay after calcination at 400^oC gives good results in terms of the bleaching power, which values equivalent to 83% (Al-Zahrani, 1995).

2.7.2 Microwave Treatment

Microwave-heating techniques are now widely used in various engineering applications including organic and inorganic synthesis (Tyagi et al., 2006; Korichi et al., 2009). Korichi et al., (2009) studied the effect of acid activation under microwave irradiation on the textural and structural properties of a smectite from Maghnia (Algeria). The results show that, the specific surface area, micropore and mesopore of smectite increases with increasing irradiation time. Therefore, the irradiation power affects the textural characteristics and surface chemistry of smectite. Korichi et al., (2009) also reported that the temperature and time required by the microwave-heating method for preparing adsorbents are far shorter than by the conventional thermal activation method. Their findings indicated that, the method is simple, economic, time saving and energy efficient. Clark et al., (2000), have discussed the advantages associated with the microwave processing to be: (a) rapid and uniform heating; (b) selective heating of microwave absorbing phases and components in materials and products; (c) decreased sintering temperatures; (d) enhanced physical and mechanical properties; (e) efficient processing of complex shapes; and (f) controlled rates and extent of processing. These advantages are not observed in the conventional processes. The authors have suggested that further research and fundamental point of view towards the microwave processing techniques will lead to a more effective and efficient manufacturing of a wide range of applications and products (Clark et al., 2000).

Deng & Lin, (1997) stated that more studies on the fundamental aspects of the microwave heating method for solid dispersion are needed in order to optimize the synthesis process. Such studies should include investigation of the effects of heating atmosphere, microwave power and different casket materials on the heating curves, ending temperature and dispersion of the active species. Baldassari et al., (2006)

synthesized organoclays using both conventional–hydrothermal and microwave hydrothermal processes, in order to compare the results obtained with two different heating methods under the same reaction conditions. The author conducted several experiments on an organic derivatization with the octadecyl-trimethylammonium cation. The results showed that the intercalation was almost completed after 2 h irradiation in the microwave oven. However, with conventional heating, the intercalation was completed only after a 6 h treatment. This proves that the microwave–hydrothermal procedure is distinctly superior to the conventional–hydrothermal processing, as a complete conversion of the original clay can be achieved in shorter reaction times (Baldassari et al., 2006). Yapar, (2009) stated that the use of microwave for drying purposes will cause a further reduction in the required time. Application of microwave irradiation at 360 W for 5 min is enough to achieve a 70% exchange efficiency which is comparable to the organic cation exchange efficiencies reported using conventional techniques. The author concluded that the use of microwave irradiation in the synthesis of organoclays is beneficial since almost the same exchange efficiency was obtained in a very short time in comparison to the conventional hydrothermal technique (Yapar, 2009).

The modification of layer charge in smectites by conventional and microwave heating treatment was conducted by Zemanová et al., (2006). They stated that the microwave heated dispersions show slightly higher layer charge reduction than conventionally heated samples where no significant changes of the layer charge were observed. Moreover, the infrared spectroscopy shows that the products obtained with microwave treatments correspond well to the materials heated conventionally for much longer periods of time. Hence, by applying microwave treatment, the time and energy required can be significantly reduced (Zemanová et al., 2006).

Gunawan et al., (2010) investigated the effect of organo-bentonite for the purification of vegetable oils by using normal heating and microwave-irradiation method. They found that, by microwave-irradiation method, the amounts of free fatty acid (FFA) removed during bleaching process are higher than the conventional heating. However, a significant decrease in peroxide value (PV) was observed for both methods, of microwave-irradiation and conventional heating (Gunawan et al., 2010).

2.8 Optimum operating conditions

Despite numerous papers published on activation of bleaching earth, there is still diminutive information on a full study pertaining to the optimum and effective parameters for obtaining the highest bleaching capacity. Therefore, a technique known as design of experiments (DOE) especially response surface methodology (RSM) is a powerful and effective technique for process characterization, optimization and modeling. The technique involves the process of planning and designing an experiment. The collected data is subsequently analyzed and interpreted. The approach using this technique is to reduce the number of experiments, improve statistical interpretation and locate the optimum parameters for acid activation (Gulsah Kirali & Lacin, 2006; Rozic et al., 2010; Didi et al., 2009). As with most processing techniques, several variables could affect the performance of bleaching earth. However, a detailed study on the DOE technique cannot be presented due to the lack of investigation on the variables using this technique.

There are many factors influencing the bleaching performance including type of adsorbent used, adsorbent dosage, effect of time and bleaching temperature, effect of vacuum, effect of agitation, oil retention, effect of moisture and effect of particle size. These factors have been reviewed by some researchers such as reviews by Bockish

(1998); King (1948); Rich (1967); Richardson (1978); Patterson (1976); Morgan (1985); Zschau (1987) and Brekke (1980). However, in the following sub-sections the most effective parameters on the activation treatment are discussed.

2.8.1 Parameters affecting the treatment techniques

2.8.1.1 The effect of acid concentration

This parameter has a significant effect in order to enhance the bleaching capacity in the edible oil treatment. A study by Didi et al., (2009) investigated the effects of activation parameters, namely acid concentration, contact time and solid/liquid ratio by using factorial experimental design in order to enhance the bleaching capacity in the colza oil treatment. The bleaching capacity was chosen for the process response. It could be seen that the acid concentration and activation time influence the bleaching capacity of bentonite greatly. The results indicated that, the highest bleaching capacity for acid activation of Algerian bentonite was 99% under optimum activation conditions when acid concentration used was 11.6 N H_2SO_4. However, an increase in the acid concentration beyond this limit would not result in any significant change in the bleaching capacity. This is due to the collapse of the clay mineral structure followed by a substantial decrease of the specific surface area. This, in turn, results in a reduction in the bleaching capacity (Didi et al., 2009). Another study by Makhoukhi et al., (2009), using factorial experiment design, the highest bleaching capacity for Algerian bentonite was found to be 99% under optimum acid concentration (12.8 N H_2SO_4). A similar observation was made by Woumfo et al., (2007) where with increasing acid concentration, the bleaching capacity increases to maximum, after which it decreases. The results indicated that the concentration below than 0.7 N HCl seemed insufficient for the attainment of maximum efficiency within 4 h. Whereas, concentration of more than 1 N HCl becomes more and more ineffective due to the excess of protons that

destroy the phyllosilicate of the material. Therefore, the maximum efficiency of the smectite clay samples is obtained after activation with 0.7 N HCl and 1 N HCl (Woumfo et al., 2007).

Myriam et al., (1998) studied the structural and textural modifications of palygorskite and sepiolite under acid treatment. The author reported that an increase in acid concentration resulted in a progressive destruction of the structures of palygorskite and sepiolite. They also observed that the greatest specific surface area obtained for sepiolite was at 3 N HCl and for palygorskite at 9 N HCl (Myriam et al., 1998). Suarez Barrios et al., (1995) demonstrated that a significant increase in specific surface area of the activated palygorskite was observed with the more dilute solution used (> 1.0 N HCl). Zhansheng et al., (2006), investigated the effects of the acid concentration in activation on the performance of the acid activated clay in the bleaching of cottonseed oil. In their research, bentonite clay was treated with 5.6, 7.5, 9.4, 11.3, 15.0 and 16.9 N H_2SO_4. They observed that the maximum bleaching capacity was obtained when bentonite clay was treated with 9.4 N H_2SO_4, with values equivalent to 70.3%, 73.1%, 83.2%, 81.8% and 88.9% respectively. Further increase in acid concentration, would not result in any significant change in the bleaching capacity (Zhansheng et al., 2006).

Gonzalez et al., (1989), reported with increasing acid concentration and reaction time, the condensation of the silanol groups increased and, thus, the microporosity and the specific surface area also decreased. The specific surface area of the magnesic palygorskite reached a maximum, 399 m^2g^{-1}, three times that of the original sample after treating with 2 N HCl and decreased smoothly with increasing acid concentration until, at 6 N HC1 for 24 h, a drastic decrease of the specific surface, 197 m^2g^{-1}, was observed. Moreover, the total volume of adsorbed N_2, increased to 0.538 cm^3g^{-1} after

the acid treatment until the concentration reached 2 N HC1 and remained constant with more severe acid treatment (Gonzalez et al., 1989).

In a research article by Rozic et al., (2008), response surface methodology (RSM) method based on central composite rotatable design (CCRD) was used to optimize the operating parameters of acid activation of bentonite which include temperature, time, acid concentration, solid-to-liquid ratio and stirring rate. The results of the acid activated bentonite were expressed in terms of the specific surface area, as the response function in the investigated process. The author reported that an increase in acid concentration greatly increased the specific surface area of the activated bentonite clays from 63.4 m^2g^{-1} to 202 m^2g^{-1}. They observed that the maximum specific surface area of activated bentonite was obtained when the temperature and acid concentration were increased simultaneously. Their results show that textural characteristics such as specific surface area and pore volume of acid activated bentonite are strongly affected by the activation parameters. They have suggested that an adsorbent with optimal porosity and good adsorption properties can be produced by chemical treatment of the bentonite clay (Rozic et al., 2008).

A similar trend was observed by Novakovic et al., (2008) and Rozic et al., (2008), where specific surface areas increased greatly in activated bentonite clays with values up to 238 m^2/g, three times higher than the surface area of natural bentonite clays (63 m^2/g). This phenomenon is corroborated by the work of Vicente Rodriguez et al., (1995) who observed that an increase in acid concentration resulted in a significantly increase in the specific surface area of the activated saponite from 35 m^2g^{-1} to 367 m^2g^{-1}. A similar observation was made by Vicente Rodriguez et al., (1994) where an

increase in acid concentration resulted in a significant increase in the specific surface area of the activated sepiolite.

Panda et al., (2010), investigated the effect of the acid treatment on the structural and chemical properties of kaoline clay. The results indicated that as the acid concentration increases, the Al_2O_3, MgO CaO and K_2O contents in the acid treated material decrease progressively. Simultaneously, SiO_2 content increased with an increase in the acid concentration, of which the Si/Al ratio was increased from 0.65 to 8.09. In addition, the specific surface area and pore volume attained were also increased when acid concentration increased. The maximum specific surface area and pore volume were found to be 143 m^2g^{-1} and 1.18 cm^3g^{-1} at 20 N H_2SO_4 (Panda et al., 2010). On the other hand, Falaras et al., (1999) observed that the specific surface area of the activated Ca-montmorillonite increased from 93 m^2g^{-1} to its maximum, 107 m^2g^{-1} at 4 N H_2SO_4 and decreased to 103 m^2g^{-1} at 8 N H_2SO_4. Other figures reported by various researchers are presented in Table 2.6.

Table 2.6: Acid concentration and corresponding optimum values

Acid concentration (N)	Optimum acid concentration (N)	References
1.0-8.0	4.0	Falaras et al., 1999
1.0-7.0	5.0	Suarez Barrios et al., 1995
3.0-6.0	6.0	Novakovic et al., 2008
2.0-7.0	4.5	Rozic et al., 2010
1.0-3.0	1.0	Gulsah Kirali & Lacin, 2006
9.0-13.5	11.6	Didi et al., 2009
10.5-13.5	12.8	Makhoukhi et al., 2009
5.6-16.9	9.4	Zhansheng et al., 2006
0.4-6.5	0.4	Vicente Rodriguez et al., 1994
1.0-6.0	2.0	Gonzalez et al., 1989
2.0-20	20	Panda et al., 2010

2.8.1.2 Treatment Time

In the work by Rozic et al., (2008), the highest leaching of MgO from Serbian smectite clay was determined using factorial and orthogonal central composite design methods. The results indicated that the leaching yield of MgO depends significantly on the acid concentration and reaction time. This is in agreement with the work of Novakovic et al., (2008), who asserted activation time has a significant effect in the leaching yield of MgO from smectite clay. The results revealed that the highest leaching yield of MgO was found to be 41.86% at 3 h activation time. Whereas, the lowest leaching yield of MgO was obtained at 1 h activation time. Foletto et al., (2003), reported that the increase in treatment time and acid concentration resulted in a more effective attack on the clay structure, as observed by the decrease in the relative amount of octahedral

cations (Al, Mg and Fe). Hence, these parameters resulted in an increase on the bleaching efficiency (Foletto et al., 2003).

Vicente-Rodriguez et al., (1996), have investigated the structural changes of sepiolite, palygorskite and two saponites occuring during the acid treatment using the FT-IR spectra. The results indicated that 56.29% of the Mg(II) cations were removed when saponite was treated with 0.4 N HC1 for 6 h at 25^{o}C. When the time of treatment was extended to 48 h, 75.22% of the Mg (II) was removed. The sample treated with 0.8 N HC1 for 48 h has a maximum value of the BET surface area, 392 m^2 g^{-1}. The results showed that Mg(II) cations removed were around 83.8% when griffithite was treated with 0.4 N HCl for 24 h and the amount increased to 100% if treated with 0.8 N HC1 for 24 h. Similarly with saponite, the maximum value of the BET surface area was obtained at 0.8 N HC1 for 48 h, of which value is equivalent to 367 m^2 g^{-1}. In addition, by treating the sepiolite sample with 0.8 N HC1 for 6 h, 42.4% of the Mg(II) cations were removed. Whereas, 100% of the Mg(II) cations were removed when it was treated with 1.6 N HCI for 48 h.The maximum in the BET surface area, 549 m^2 g^{-1}, was reached after treatment with 0.4 N HC1 for 48 h. For palygorskite, 50.3% of the Mg(II) cations were removed after treatment with concentration (3 N), activation time (1 h) and at 90^{o}C temperature. Whereas, 99% was removed if 7 N HC1 was employed. The sample treated with 5 N HC1 displayed a maximum value of the surface area, 286 m^2 g^{-1}. It could be seen that activation time influenced the dissolution rate of octahedral cation greatly (Vicente-Rodriguez et al., 1996).

Woumfo et al., (2007) studied the effect of activation parameters of Cameroonian smectite clays on its bleaching capacity. The results indicated that by increasing the activation time from 2 to 8 h, the removal of carotene increases to a maximum, after

which it decreases. This was due to the progressive destruction of phyllosilicates and acid centres (Woumfo et al., 2007). Gulsah Kirali & Lacin (2006) studied the effect of activation parameters of Turkish bentonite clay on its bleaching capacity by using full factorial design. The highest bleaching capacity was obtained for clay activated for 6 h activation time, whereas the lowest bleaching capacity was obtained for 2 h activation time. The results reveal that with increasing activation time, the bleaching capacity increases to a maximum. Makhoukhi et al., (2009), studied the effect of three parameters namely; temperature, contact time and acid concentration on the bleaching capacity of an Algerian bentonite in colza oil processing. They reported that among the parameters investigated, acid concentration and activation time greatly influence the bleaching capacity of bentonite. Didi et al., (2009) reported that a maximum bleaching effectiveness was obtained for an activation time of approximately 9 h. Beyond this values, a significant reduction in bleaching activity was observed and resulted in a significant decrease in the specific surface area and structure porosity (Didi et al., 2009).

Srasra & Trabelsi-Ayedi (2000) have proven that the specific surface area, the porosity and microporosity of acid activated glauconite are strongly affected by the activation time. They observed that with increasing activation time, the specific surface area, the porosity and the microporosity obtained also increases. However, the maximum bleaching efficiency of rapeseed oil is not associated with maximum activation time (Srasra & Trabelsi-Ayedi 2000). This result is further supported by a research from Franus et al., (2004) in which textural parameters of the glauconite increased with the activation time. The results show that the specific surface area increased from 78 m^2g^{-1} in natural glauconite to 329 m^2g^{-1} after longer activation time. This effect was also reported by Christidis et al., (1997) where the optimum conditions for activation can be

achieved by varying the combinations between acid concentration and activation time. They concluded that the optimum bleaching capacity of rapeseed oil does not follow the variations of the specific surface area (Christidis et al., 1997). The reaction time and corresponding optimum values are summarised in Table 2.7.

Table 2.7: Reaction time and corresponding optimum values

Treatment time (h)	Optimum treatment time (h)	References
1.0-7.0	7.0	Franus et al., 2004
0.5-7.0	4.0	Srasra & Trabelsi-Ayedi, 2000
2.0-6.0	6.0	Gulsah Kirali & Lacin, 2006
6.0-12.0	10.0	Didi et al., 2009
2.0-3.5	2.0	Foletto et al., 2003
1.0-3.0	3.0	Novakovic et al., 2008
1.0-3.0	3.0	Rozic et al., 2008
4.0-8.0	7.0	Makhoukhi et al., 2009
2.0-48	48	Vicente-Rodriguez et al., 1996
2.0-48	24	Vicente-Rodriguez et al., 1996
2.0-48	48	Vicente-Rodriguez et al., 1996

2.8.1.3 The Effect of Temperature

Novak & Cicel, (1978) showed that the best correlation was found between the decomposition rate expressed as the halftime of dissolution and the octahedral substitution in dioctahedral smectites. The decomposition rate of dioctahedral smectites

in 6 N HCI at 96^{o}C, increases with increasing substitution of Mg^{2+} and Fe^{3+} content in octahedral sheets. It can be seen that temperature influences the dissolution rate of the octahedral cations (e.g. Mg^{2+} and Fe^{3+}) (Novak & Cicel, 1978).

Rozic et al., (2008) revealed that temperature, leaching time and acid concentration exert the strongest influence on the specific surface area of smectite. They reported that the highest leaching yield of MgO was obtained at 90^{o}C, whereas the lowest leaching yield of MgO was attained at 70^{o}C. However, the temperature does not seem to significantly influence the leaching yield of MgO (Rozic et al., 2008). Makhoukhi et al., (2009) proved that the temperature had no significant individual effect on the activation of bentonite. The results revealed that the optimum bleaching capacity was obtained at temperature 90^{o}C. Therefore, between 90^{o}C and 120^{o}C, the phase temperature does not seem to significantly influence the bleaching capacity of the bentonite (Makhoukhi et al., 2009). The work of Al-Zahrani et al., (2001), stated that the activation reaction does not proceed to any appreciable degree at low temperatures. The results showed that the highest bleaching power was found to be 101% after 0.25 h activation at 120^{o}C and the lowest bleaching power was attained after 1 h activation at 22^{o}C, which values equivalent to 8%.

Balci (1999) reported that the maximum specific surface area and textural properties of the sepiolite were obtained at 100^{o}C and decreased with further treatment of temperature to 200^{o}C. In contrast, Rozic et al., (2008) reported that temperature and activation time had a highly significant effect on the specific surface area and textural properties of the acid activated bentonite. They showed that the maximum specific surface area of activated bentonite was obtained when the temperature and acid concentration were increased simultaneously. At high temperature phase and low acid

concentrations, high specific surface areas were achieved (Rozic et al., 2008). When glauconite was activated by HCl at 60^{o}C, there was progressive dissolution of the octahedral layer. Moreover, the specific surface area and textural properties of activated glauconite depend on the activation temperature. It was observed that the BET surface area was found to be 131 m^2g^{-1} after 3 h activation at 60^{o}C and 186.7 m^2 g^{-1} was obtained after 3 h activation at 100^{o}C (Franus et al., 2004). A similar trend was observed for the volume of micropores and mesopores. The temperature and corresponding optimum values are summarised in Table 2.8.

Table 2.8: Temperature and corresponding optimum values

Temperature (^{o}C)	Optimum temperature (^{o}C)	References
100-900	100	Balci, 1999
70-90	90	Novakovic et al., 2008
70-90	90	Rozic et al., 2008
63-97	90	Rozic et al., 2010
60-120	90	Makhoukhi et al., 2009
96	96	Novák & Číčel, 1978
22-120	120	Al-Zahrani et al., 2001

2.8.1.4 Solid to liquid ratio

According to Didi et al., 2009, when the solid to liquid ratio is increased from 260 to 340 g/L, it resulted in a slight increase in the bleaching capacity from 97.5 to 99%. However, this parameter would not result in any significant change in the bleaching capacity. Therefore, this parameter is indicated as the weakest influence, as compared to the other parameters (Didi et al., 2009). A similar observation was made by Rozic et al., (2008) where solid to liquid ratio did not show a strong influence on the specific surface

area of smectite, as compared to other parameters. Al-Zahrani et al., (2001) studied the effect of solid to liquid ratio on the bleaching power of the bentonite clay. The results revealed that when the solid to liquid ratio were increased to 0.05 g/L, the bleaching power of activated clay also increased, whereas further increase to 0.07 g/L resulted in a decrease in the bleaching power. Therefore, the best result of solid to liquid ratio was obtained at 0.05 g/L. At low solid to liquid ratio, the contact between the acid and the clay is lesser than when the ratio is high and the rate of reaction is slow (Al-Zahrani et al., 2001). However, this parameter has a small effect on the bleaching power compared to the effects of acid concentration, activation time and temperature.

Novakovic et al., (2008) showed that an increase in the solid to liquid ratio resulted in an increase of the leaching yield of MgO. This effect was reported by Rozic et al. (2008) where among the parameters investigated, solid to liquid ratio, acid concentration and stirring rate had significant effect. In contrast, Gulsah Kirali & Lacin, (2006) observed that the highest bleaching capacity is attained at 500 g/L solid to liquid ratio, whereas the lowest bleaching capacity was obtained at 100 g/L solid to liquid ratio. The results indicated that solid to liquid ratio has a significant effect on the bleaching capacity.

2.8.1.5 Moisture content

According to Rich, (1967) bleaching earth normally contains between 10-18% free moisture. If clay is dried prior to bleaching, the layers collapse, resulting in impaired bleaching power because of decrease in the specific surface area. However, in bleaching, the colour bodies cannot be adsorbed to the clay's maximum capacity until its free moisture has been removed by heating.

Gulsah Kirali & Lacin (2006) observed that the highest bleaching capacity obtained for bentonite was at 4% moisture, whereas the lowest bleaching capacity attained was also at 4% moisture. They noted that the increase from 4-8% in the moisture of bentonite had no significant effect on bleaching capacity of the cottonseed oil. Oboh & Aworh, (1988) stated that with increasing acid concentration, the moisture content at which maximum percentage colour reduction is obtained, decreases for clay activated with Sulphuric acid (H_2SO_4) and acetic acid (CH_3COOH). However, with increasing acid concentration, the moisture content at which maximum percentage colour reduction is obtained, increases for clay activated with HCl. The author showed that the highest colour reduction for clay activated with H_2SO_4 and HCl was attained at 11.02% and 13.37% moisture, which is equivalent to 93.07% and 92.99%. Whereas the highest colour removal was found to be 45.59% for clay activated with CH_3COOH at 12.06% moisture. Therefore, the results revealed that the highest colour removal is not associated with the maximum moisture content (Oboh & Aworh, 1988).

2.9 Summary

In this chapter, textural characteristics, surface chemistry and various activation techniques of bleaching earth have been presented. However, despite numerous publications in literature on the bleaching earth, there is still diminutive information on a full study pertaining to the relationship between porous morphology and surface chemistry of bleaching earth. The literature review shows that there is a need for a more detailed systematic study on the surface chemistry, focusing mainly on the active sites or functional groups and some technical improvements in the adsorption processes. In addition, the performance of bleaching earth is also depending on the activation treatment which results in structural modifications. Therefore, it is very important to monitor the structural and textural modification of bleaching earth which occurs during

acid, basic, organic, thermal and pillaring treatment. However, there are several parameters that affect the effectiveness of these treatments such as, type of acids used, acid concentration, temperature, reaction time, particle size and moisture content. Although much has been accomplished in the areas of bleaching earth, a great deal of work is necessary (i) to make in depth study on a new techniques that are more environmental friendly (ii) to investigate a new alternative source for the bleaching earth (iii) and to investigate an effective technique for the bleaching earth that can be used for the purification of vegetable oils.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Introduction

This chapter describes the experimental design and methods of characterisation for the modification of bleaching clay. The natural clay and acid activated clays were analysed by various techniques: X-ray Fluorescence (XRF), X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), BET Surface Area and Scanning Electron Microscope (SEM). The methods used to determine the quality of bleached palm oil such as free fatty acids (FFA), peroxide value (PV), Lovibond colour, phosphorus, carotene content, oil retention and filtration time are also described.

3.2 Materials

Crude palm oil (CPO) was provided by Sime Darby Jomalina Sdn. Bhd., Malaysia. The commercial activated clay used for comparison was obtained from Taiko Clay Sdn. Bhd., Malaysia. This material is bentonite clay, which has been activated with sulphuric acid. K-10 montmorillonite clay, sulphuric acid (96%) and hydrofluoric acid (54%) were purchased from Fisher Scientific Sdn.Bhd., Malaysia. All chemicals used in the experiments were of analytical grade.

3.3 Experimental Methods

3.3.1 Preparation of Acid Activated Clays

K-10 montmorillonite clay was dried in the oven at 105ºC for 2 hours. Subsequently, it was ground by using an electric grinder to achieve particle sizes smaller than 63 µm prior to activation.

The activation with sulphuric acid was carried out under atmospheric pressure in a jacketed glass reactor equipped with a reflux condenser, a stirrer and a thermometer sensor. Meanwhile, the activation with hydrofluoric acid was first prepared in a Teflon plastic bottle, and then bathed in water, which was held in Pyrex glass for the purpose of heating on a hot plate. 100 ml of 2, 3, 4, 5 and 6 M sulphuric acid (H_2SO_4) or hydrofluoric acid (HF) solution were added respectively into the reactor that contained 20 g of montmorillonite clay in the ratio of 1:5 (w/v). The reaction temperature was maintained at 90^{o}C for 1, 2, 3 and 7 hours with constant stirring (450 rpm). After reflux, the clay suspension was washed repeatedly with distilled water until it reached the pH of supernatant (4-5). The acid-activated clay was filtered in a Buchner funnel and dried at 105^{o}C for 3 hours. The dried clay was then crushed into particle sizes that would pass through a 63 µm and was kept in a desiccator containing silica gel.

Physical and chemical properties of the acid activated clays were evaluated by moisture content, XRF, XRD, FTIR, BET surface area and SEM. Acid activation experiments were carried out twice in order to get good average results. Schematic diagram of activation using sulphuric and hydrofluoric acid are presented in Figures 3.1 and 3.2. In addition, the flowchart of acid activation clay is given in Figure 3.3.

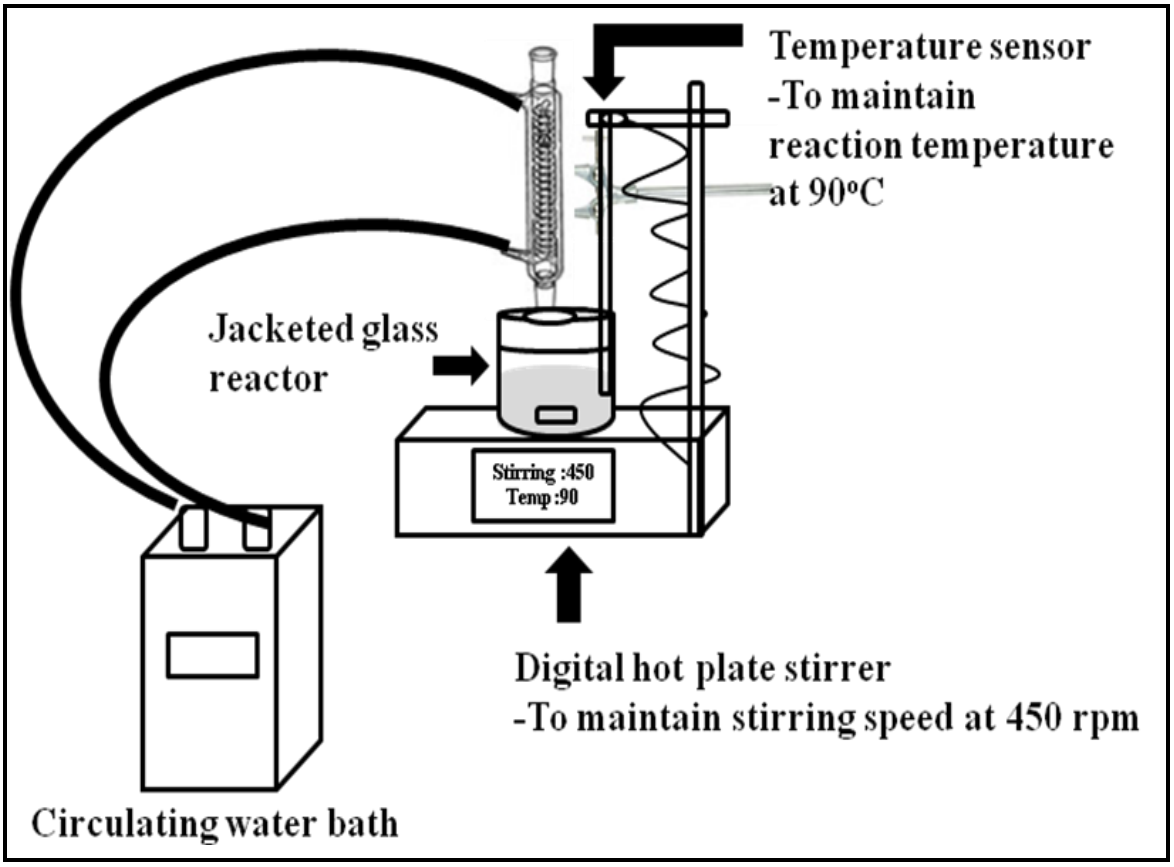


Figure 3.1: Schematic diagram of the modification of bleaching clay using H_2SO_4

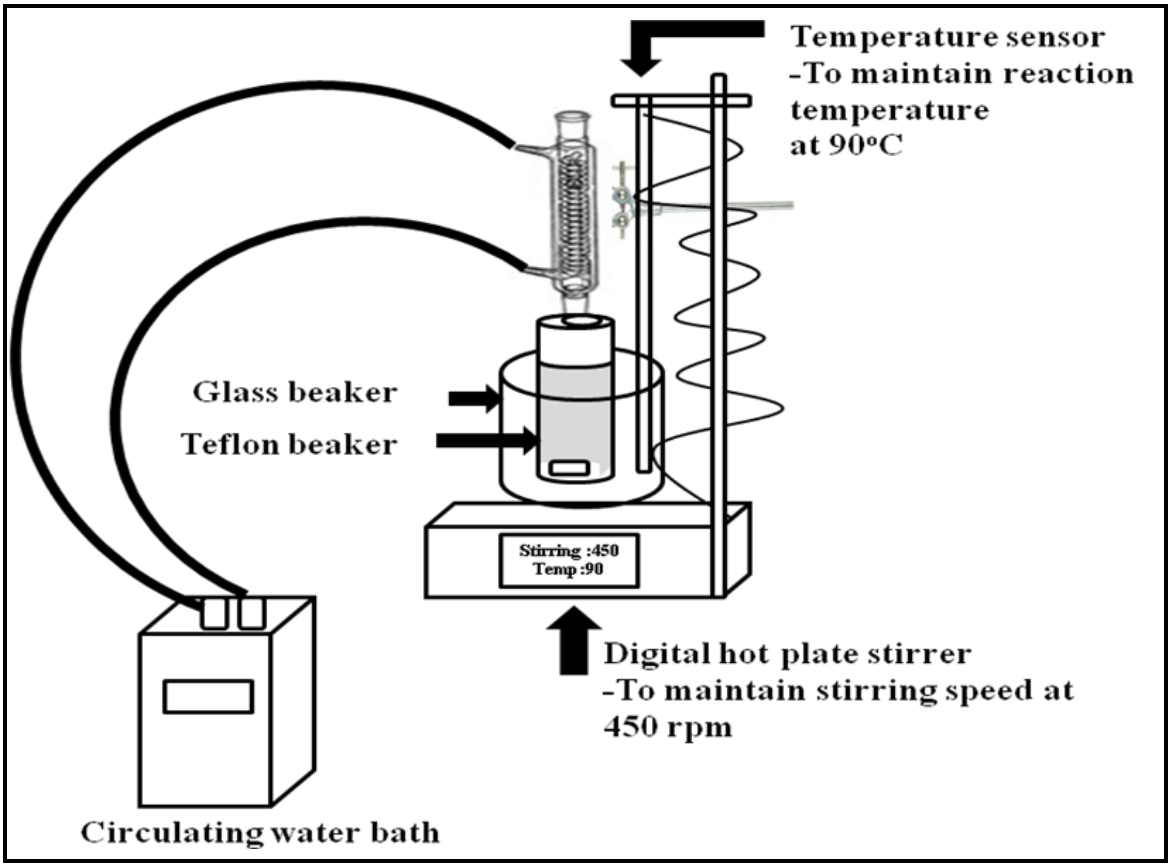


Figure 3.2: Schematic diagram of the modification of bleaching clay using HF

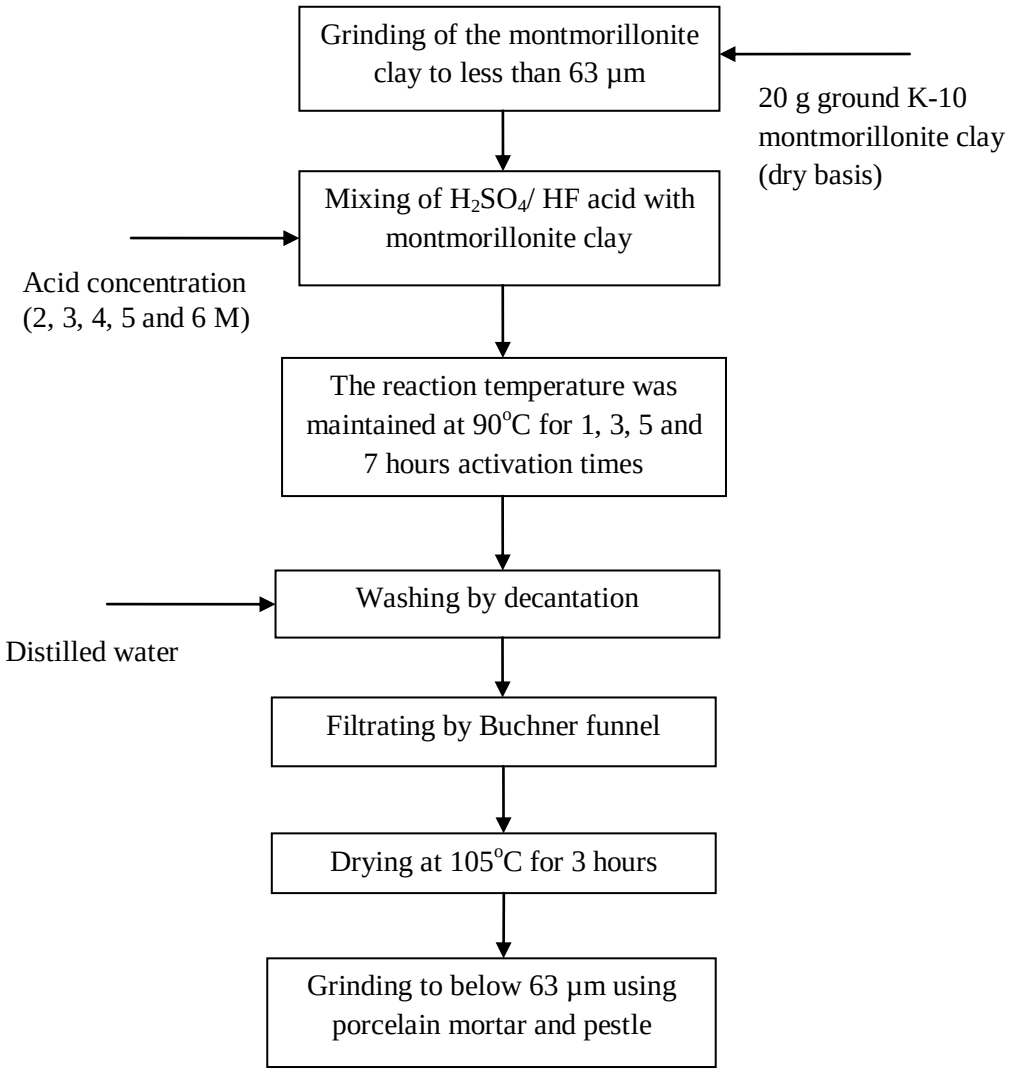


Figure 3.3: Flowchart of acid activation clay

3.3.2 Laboratory-Scale Physical Refining (Preparation of Degumming Process)

Firstly, the sample of crude palm oil (CPO) was heated to a temperature of 60^{o}C in an oven to totally melt the oil before it was transferred into degumming flask. The degumming process was performed in a 500 mL two-neck flat bottom flask at a temperature of 85°C under vacuum (30 mm Hg pressure) with stirring rate of 500 rpm. Then, approximately 0.04% (w/w basis) of phosphoric acid (85% concentration) was added with constant stirring for 20 minutes.

3.3.3 Preparation of Bleaching Process

After the degumming process, the temperature of the sample was increased to 95^{o}C. Approximately 1% (w/w basis) of the bleaching earth was then added into the sample. The bleaching process was maintained at 95^{o}C, under vacuum (30 mm Hg pressure) with constant stirring for 30 minutes at 500 rpm. Then, the bleached oil was filtered under suction using Whatman No.1 filter paper and the product obtained is called the Bleached Palm Oil (BPO). The experimental flowchart of degumming and bleaching process is shown in Figure 3.4.

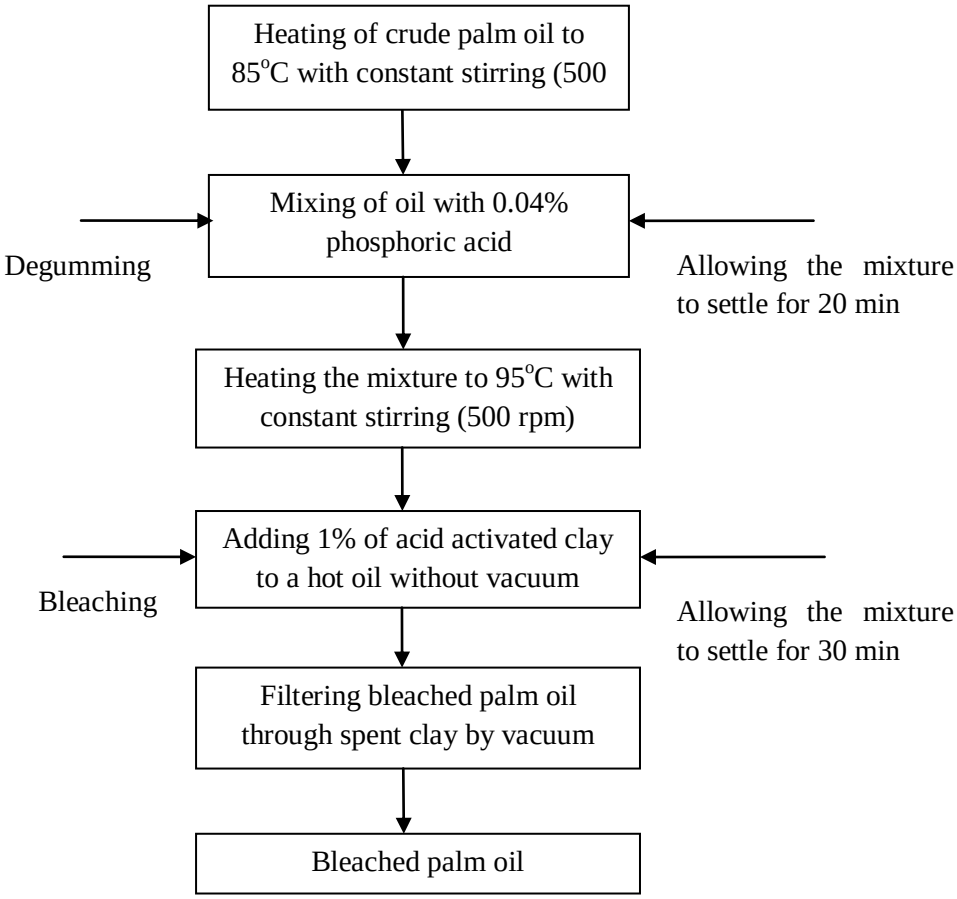


Figure 3.4: Experimental flowchart of degumming and bleaching process

3.4 Characterisation of acid activated clay

3.4.1 Moisture

10.0 ± 0.2g prepared sample was weighed and dried in the oven to a constant weight at temperature 105 ± 5°C. Finally, sample was cooled in desiccators for 20 min and weighed.

3.4.2 X-ray Fluorescence Analysis

The chemical compositions of the natural, commercial and acid-activated clay were determined using X-ray fluorescence (XRF). The analyses were performed on a Bruker S4-EXPLORER XXF equipped with a SPECTRA^{PLUS} V1.64 computerized control unit. The resulting elements (i.e. Ca, Mg, Al, etc) were translated into their oxide forms (i.e. CaO, MgO, Al_2O_3 etc) to represent the final composition.

3.4.3 X-ray Diffraction Analysis

Presence of crystalline forms and the compound phases in the natural, commercial and acid activated clay samples were determined by X-ray diffraction (D8 Advance X-Ray Diffractometer-Bruker AXS) using Cu-K_α monochromatized radiation, operating at 40 kV and 40mA with a scanning speed of $1^o 2\Theta$/min in the interval between 10^o to 70^o degree.

3.4.4 Fourier Transform Infrared Spectroscopy Analysis

The chemical structures of natural and acid activated clay samples were characterized by FT-IR spectrometer (Perkin Elmer, Spectrum 400). Dry solid samples were pressed into a disc with KBr. The samples were scanned in the range of 550-4000 cm^{-1} with a resolution of 4 cm^{-1}.

3.4.5 Specific Surface Area (BET) Analysis

The specific surface area (BET) was measured through nitrogen adsorption at 77 K data, using the Brunauer-Emmet-Teller (BET) method with a Quantachrome Autosorb-1 instrument. The BET surface area was evaluated in the range of p/p^o from 0.05 to 0.20. The samples were outgassed 24 h under vacuum condition at 95^{o}C.

3.4.6 Scanning Electron Microscope Analysis

The morphology of clay samples was investigated by scanning electron microscope (SEM) with a FEI Quanta 200 FESEM instrument operating at 2 kV-5 kV.

3.5 Characterisation of palm oil bleaching

3.5.1 Free Fatty Acids (FFA)

The free fatty acids (FFA) content in the oil can be determined by using titration method according to the PORIM Test Methods (1995). The weight of oil sample was measured in a conical flask in the range of 1 to 3 g. The isopropanol alcohol (IPA) was mixed together with 2 to 3 drops of phenolphthalein in the conical flask and heated with continuous stirring on the hot plate using magnetic stirrer. Potassium hydroxide (KOH) was dribbled into the flask until the colour changes to pale purple. Thereafter, 50 ml of mixture was transferred into the conical flask containing the sample of oil. Finally, the mixture was heated again on the hot plate while continuously stirring and titrating with KOH until the colour of the mixture changes to red.

The percentage of FFA was calculated by using the equation below:

$$\text{Free Fatty Acids (FFA)}\% = \frac{25.6 \times \text{normality (N)} \times \text{titration volume}}{\text{Weight of sample}} \qquad (3.1)$$

3.5.2 Peroxide Value (PV)

The peroxide value is a measure of the substances in a sample, expressed in terms of milliequivalents of active oxygen per kilogram which oxidizes potassium iodide under conditional test. Peroxide value in the oil samples can be determined by using titration method according to the PORIM Test Methods (1995). The sample of oil was weighed in a conical flask in the range of 3 to 5 g. Thereafter, 30 ml of PV solvent and 0.5 ml of Potassium iodide were added into the mixture. The mixture was shaken for 1 minute before adding 30 ml of distilled water. 2 to 3 drops of starch were dropped into the sample as an indicator. Finally, the sample was titrated with Sodium thiosulphate (0.01N) until it forms a clear solution. The peroxide value can be calculated as:

$$\text{Peroxide Value}\,(\text{PV}) = \frac{1000 \times \text{titration volume} \times \text{normality}}{\text{Weight of sample}} \qquad (3.2)$$

3.5.3 Lovibond Colour

The colour of the crude and bleached palm oil was measured by a Lovibond Tintometer Model F and reported as Lovibond units of red and yellow. The melted oil sample was poured into a 1 inch cell and the colour was measured as described by PORIM Test Methods (1995). This technique consists of matching the colour of the light transmitted through a specified depth of oil with the colour of light transmitted from the same source through a set of coloured glass slides. Colour reading is thus subjective and depends on the analyst's judgement as well as on the type and model of colorimeter used.

The percentage removal of red colour index can be calculated using the Khrisnan equation as follows (Srasra et al., 1989).

$$\text{Colour Removal}\,(\%) = \frac{(\text{Colour of CPO}) - (\text{Colour of BPO})}{\text{Colour of CPO}} \times 100 \qquad (3.3)$$

3.5.4 Carotene

The carotene content of the palm oil is calculated as β-carotene expressed in terms of parts per million (ppm). The method is according to the PORIM Test Methods (1995). The β-carotene concentrations in the crude and bleached palm oil samples were measured by the UV-Vis spectrophotometer (Varian Cary Bio 100) at 446 nm. The β-carotene removal percentage in the bleached palm oil can be calculated using the following equation:

$$\beta\text{C Removal}\,(\%) = \frac{(\beta\text{C of CPO}) - (\beta\text{C of BPO})}{\beta\text{C of CPO}} \times 100 \qquad (3.4)$$

Where βC = β-carotene

3.5.5 Phosphorus

This analysis determines the total phosphorus content by charring and ashing the oil in the presence of magnesium oxide followed by calorimetric measurement as phosphovanadomolybdic complex. The method used is according to the PORIM Test Methods (2005). The charring step is a critical and tedious stage where precautions are required to ensure reproducibility of result. The yellow phosphovanadomolybdic complex between phosphate, vanadate and molybdate was formed and the colour was determined by the UV-Vis spectrophotometer (Varian Cary Bio 100) at 400 nm.

3.5.6 Oil retention

In the bleaching process, oil retention is required to ascertain the loss of oil due to its retention in the bleaching clay. Oil retention can be calculated as (Usman et al., 2012)

$$\text{Oil Retention}(\%) = \frac{\left(W_{\text{Filter Cake}} - W_{\text{BleachingClay}}\right)}{W_{\text{Filter Cake}}} \times 100 \qquad (3.5)$$

3.6 Statistical Analysis

Statistical analysis was carried out by Microsoft Office Excel 2007. The data were subjected to two way analysis of variance (ANOVA) to determine the significant ($p<0.001$) main and interaction effects of independent variables namely acid concentration and activation time on the response variables studied. The physicochemical properties of oil, namely red colour index were considered as the response variables. The analyses were carried out in triplicate and the results were reported as means ± standard deviations (SD).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Part 1: Characterisation of the physical and chemical properties of acid activated clays.

In this section, the physical and chemical properties of acid activated clays are discussed based on the analysis results. This will cover moisture content, X-ray Fluorescence (XRF), X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), BET Surface Area and Scanning Electron Microscope (SEM).

4.1.1 Moisture Content

Moisture is considered undesirable in bleaching of palm oil, since it contributes to the free fatty acids content and increases the oil loss during oil refining (Lomić et al,. 2004). Too much water in bleaching clay will tremendously reduce the ability of the bleaching clay to absorb colour. According to Rich, (1987) bleaching clay normally contains between 10-18% free moisture. In this study, it is indicated that the moisture content of clay activated with HF and H_2SO_4 is in the range of 9-12.1% (Table 4.1). This means that the moisture content of acid activated clays investigated in this study is suitable for bleaching of the palm oil.

Table 4.1: Moisture content (%) of the K-10 montmorillonite clay after treatment with H_2SO_4 and HF under different conditions

Acid Concentration (M)	Activation Times (h)	Moisture Content H_2SO_4 (%)	Moisture Content HF (%)
2	1	11.9	10.8
	3	11.1	10.1
	5	10.5	10.5
	7	10.3	10.3
3	1	9.5	9.2
	3	9.2	9.5
	5	10.1	9.5
	7	10.5	10.0
4	1	10.5	11.0
	3	11.5	11.5
	5	12.0	11.5
	7	12.1	12.0
5	1	11.5	10.5
	3	9.5	9.5
	5	10.5	10.5
	7	11.5	10.5
6	1	9.0	9.5
	3	9.5	9.0
	5	10.5	10.0
	7	10.1	10.5

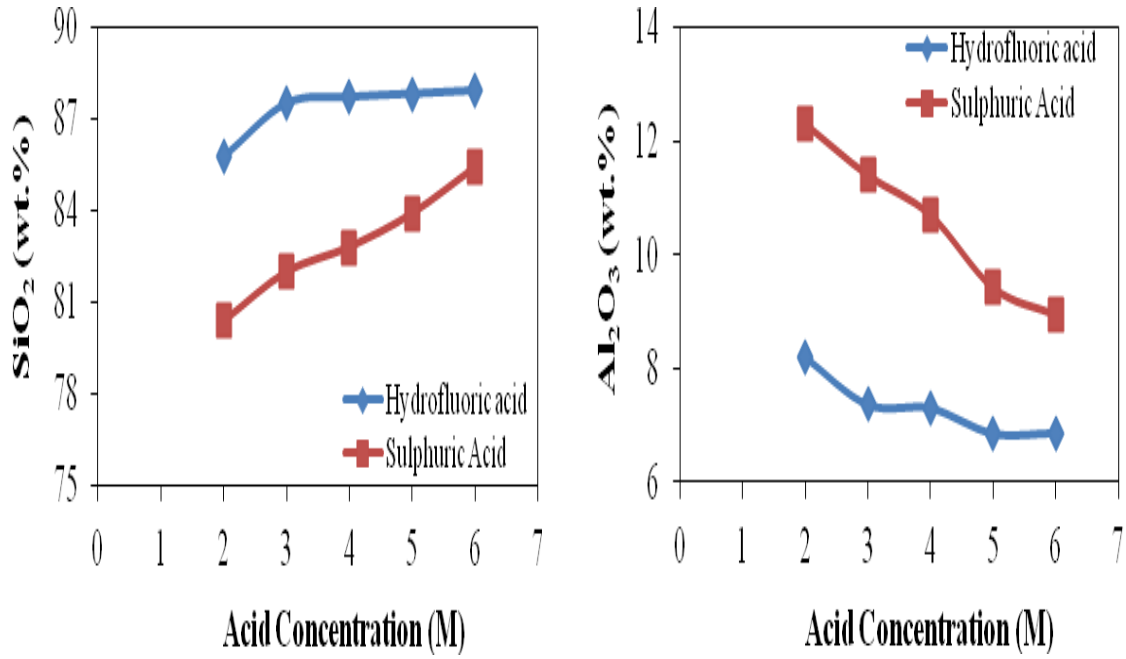
4.1.2 Chemical Composition

Figure 4.1 shows the effects of acid concentration and acid type on the chemical composition of acid activated clays. The Al_2O_3, Fe_2O_3, MgO, CaO and K_2O contents of the natural clay were 14.2, 3.28, 1.2, 0.35 and 2.03 wt.%. From Figure 4.1, it can be seen that, Al_2O_3, Fe_2O_3, MgO, CaO and K_2O contents decrease with increasing acid concentration, while silica oxide (SiO_2) content increases gradually after treatment with H_2SO_4 and HF. The percentage of SiO_2 is 77.40% for the natural clay. However, it increases to 85.40% with treatment by 6 M H_2SO_4 for 1 hour. Similarly, the percentage rises up to 87.90% after treating with HF. The SiO_2 content of the clay activated with HF was higher than that of the natural clay and H_2SO_4 activated clay. The increase in SiO_2 content can be explained by the depletion of the interlayer and octahedral cations after acid activation. The increase in SiO_2 content after acid activation was investigated by Siddiqui (1986), who reported that the high silica content might have some bearing on its decolourising efficiency.

It is observed that exchangeable cation, such as Ca^{2+}, was the easiest to be removed after treatment with low HF and H_2SO_4 acid concentration, as they are located out of the montmorillonite lattice (between layers). For both acids, the dissolution of the octahedral cations (such as Al^{3+}, Fe^{3+}, and Mg^{2+}) was continuous as the acid concentration increased from 2 M to 6 M. Meanwhile, Al^{3+} was the most difficult oxide to be dissolved by HF and H_2SO_4 activated clays, compared to Fe^{3+} and Mg^{2+}. This is attributed to the fact that, in the clay minerals structure, Al^{3+} occupies the centre of the ribbons while Mg^{2+} is located at the edges of the octahedral ribbons (Güven, 1992). Another factor that promotes the rapid decrease in Mg^{2+} content is that MgO is more soluble in acidic media than Al_2O_3. Moreover, the percentage of K_2O in the clay samples remains almost constant during the HF and H_2SO_4 acid treatment. Results show

that the dissolving order of the cations in the octahedral sheet of montmorillonite is $MgO > Fe_2O_3 > Al_2O_3$.

The results further proved that activation with HF causes some changes in the chemical composition of the activated clay samples. As reported by Steudel et al., (2009), H_2SO_4 activated clay gave the best results in dissolving the octahedral cations. However, from this study it was found that HF activated clays appeared to be a more superior acid than H_2SO_4 activated clays by showing the best results in dissolving octahedral cations. This might imply that HF activated clays have the potential to be used as adsorbents in the purification of palm oil.



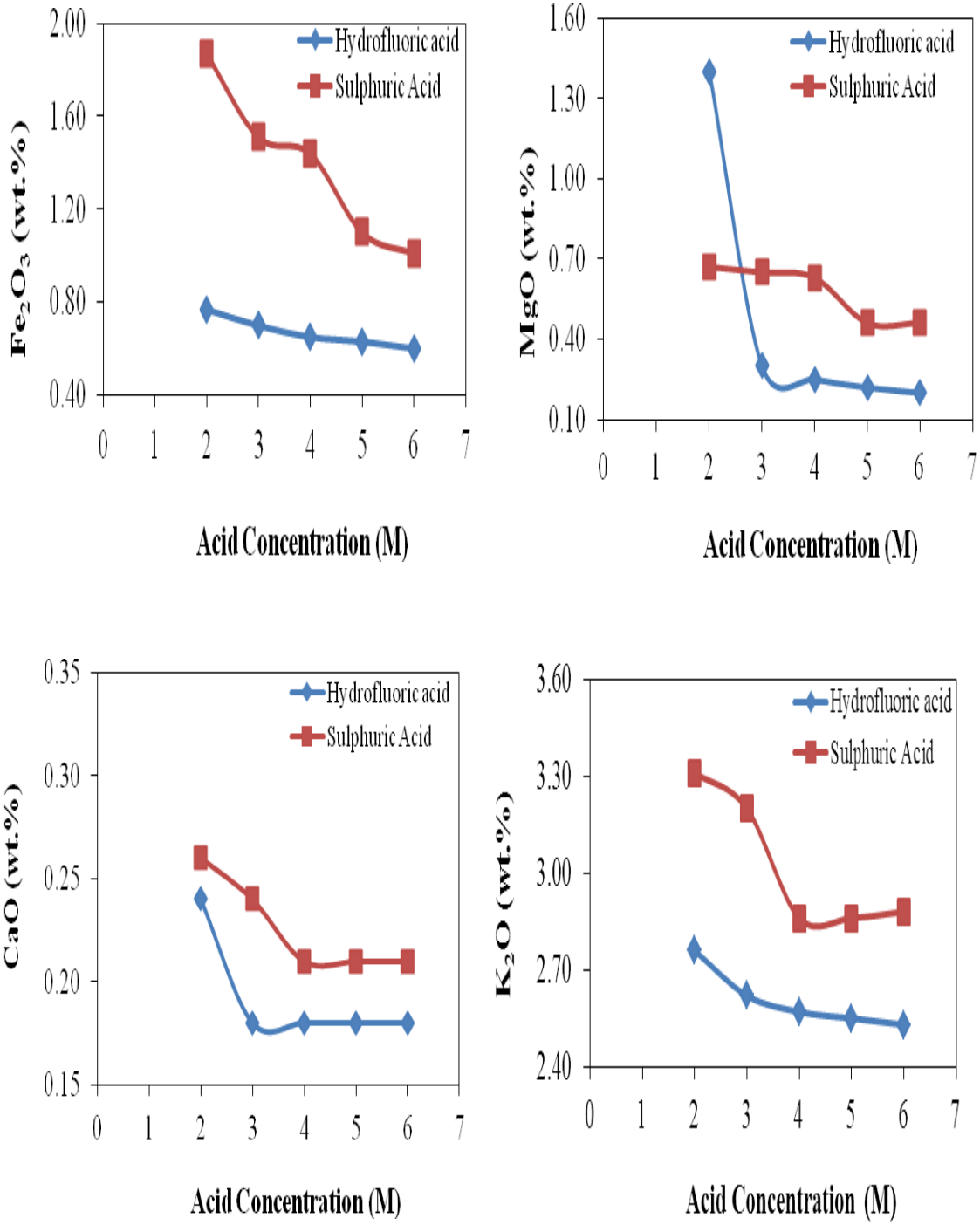


Figure 4.1: Chemical composition of K-10 montmorillonite clay after treatment with various concentrations of H_2SO_4 and HF

4.1.3 Mineralogy Composition

The XRD patterns of the natural and acid activated clays are presented in Figures 4.2 to 4.4. As shown in Figure 4.2, the presence of montmorillonite and quartz are evident in the clay samples.

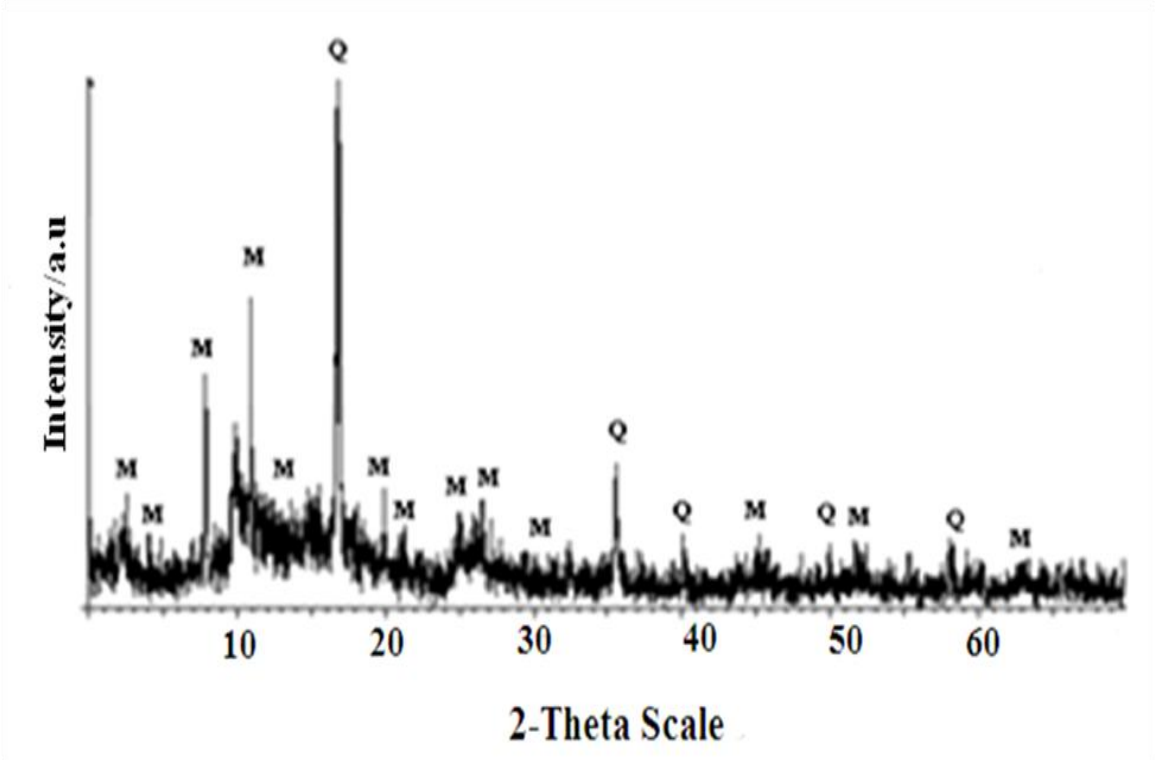


Figure 4.2: XRD patterns of the natural clay. M: montmorillonite, Q: quartz.

The XRD results observed from Figures 4.3 and 4.4 indicated that the effect of acid concentration and activation time have caused structural changes to the acid treated clays. The effect of both activation time under constant acid concentration, and acid concentration under constant activation time on the montmorillonite structure are similar. Although it seems that the variation of activation time for the chosen acid concentration (i.e. 3 M HF and H_2SO_4) shows more drastic changes.

The most pronounced modification occurred to the montmorillonite clay can be observed for the peak d(001), which shows reduction in intensity as a result of acid activation. At high H_2SO_4 concentration, the 001 basal reflections are lost, and the

presence of an amorphous silica phase is indicated by the large, broad peak appeared at 2Θ values between 15 to 35^{o}. However, for HF activated clays, the 001 basal reflections disappeared at low acid concentration. These findings are supported by the results reported by Christidis et al., (1997), where it was stated that montmorillonite peaks started to disappear and resulted in amorphous structure of montmorillonite. Nevertheless, since the montmorillonite peak still appears after 5 M acid activation, it can be assumed that the structure has only been partially destroyed. Eventually, upon acid treatment the peak intensity of the clay decreases significantly. This is due to the structural disorder that was caused by the acid treatment, which affects the crystalline character of the clay. It is also caused by the attack on the octahedral layer and the exposure of the tetrahedral layer (Eren & Afsin, 2009). These observations were also reported by several other researchers, for instance: Foletto et al., (2003) and Steudel et al., (2009).

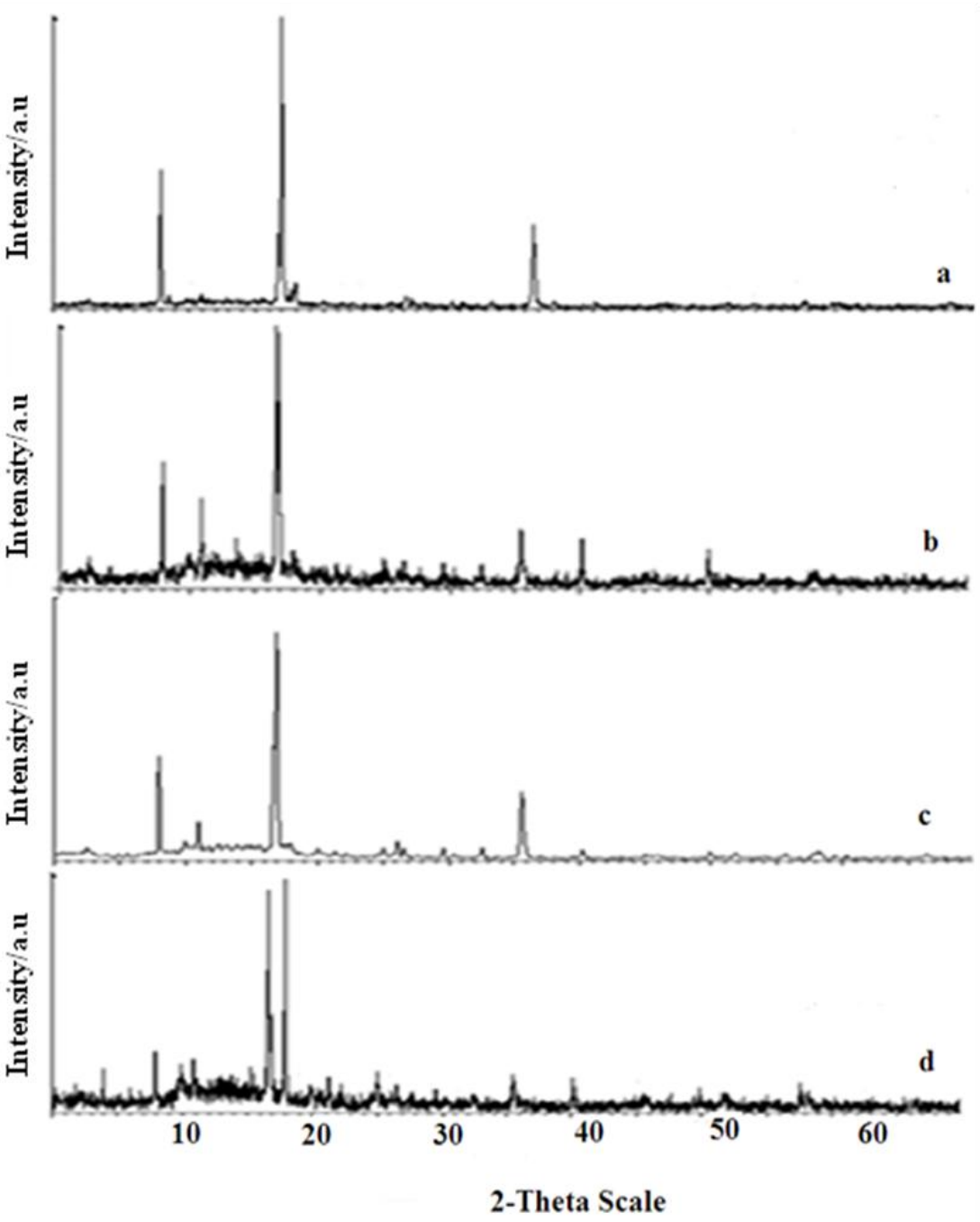


Figure 4.3: XRD patterns of clay activated with H_2SO_4 at (a) 5 M, 3 h (b) 4 M, 3 h (c) 3 M, 5 h and (d) 3 M, 3 h, respectively.

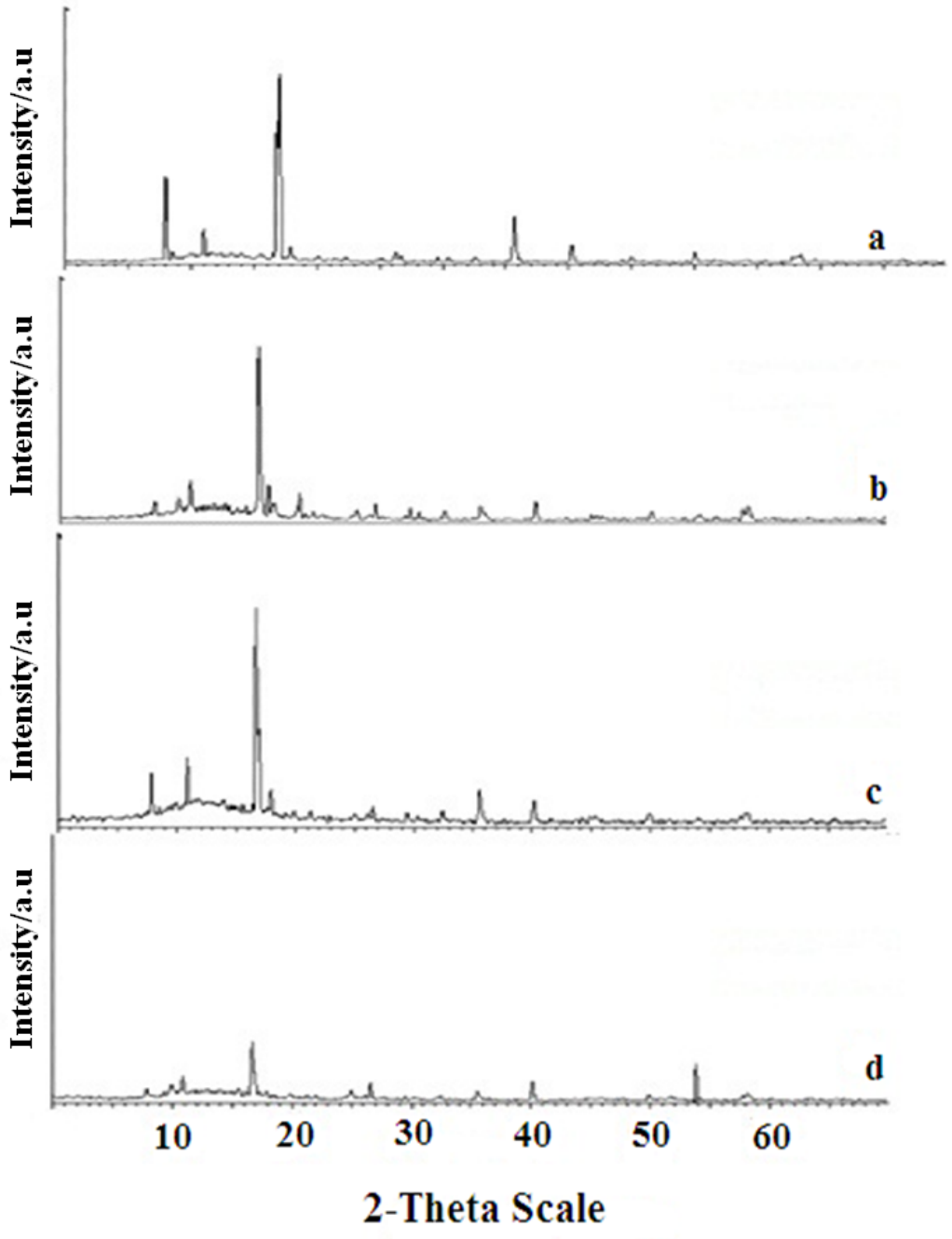


Figure 4.4: XRD patterns of clay activated with HF at (a) 5 M, 3 h (b) 4 M, 3 h (c) 3 M, 5 h and (d) 3 M, 3 h, respectively.

4.1.4 FTIR Analysis

Study of acid activated clays by FTIR spectra confirmed the dissolution of the octahedral layer and the generation of free silica when the montmorillonite structures were destroyed by acid treatment. Figures 4.5 to 4.8 present the FTIR spectra of the samples, i.e. untreated clay, clay activated with H_2SO_4 and HF. The spectra can be summarized as follows: the bands at 3622 cm^{-1} and 3408 cm^{-1} show the stretching for the ─OH groups of interlayer water molecules in the clay. The three samples, i.e. untreated clay, clay activated with H_2SO_4 and HF show this absorption. Nonetheless, it can be observed from Figure 4.7 that the intensity of the absorption band at 3408 cm^{-1} decreases and finally disappears after treatment with 4 M HF for 1 h. The band at 1637 cm^{-1} also shows the deformation vibration for ─OH groups of the absorption by the interlayer water molecules. The intensity of Si-O stretching band at 1057 cm^{-1} looks not affected by the treatment at 1057 cm^{-1}. The band for Al-O-H stretching at 914 cm^{-1} decreased with treatment of the samples and the band at 878 cm^{-1} which is assigned for the AlMgOH deformation band disappeared after acid treatment (Figures 4.6 and 4.8). This is due to the substantial leaching of the Mg^{2+} ions with the acid activation (Novakovic et al., 2008; Temuujin et al., 2004).

The IR spectra of the sample, shows that the stretching vibration modes of MgOH at 694 cm^{-1} and the band for Si-O-Al at 520 cm^{-1} disappeared with increasing acid treatment (Figure 4.8). In addition, the band at 796 cm^{-1} appeared in the untreated clay, clay activated with H_2SO_4 and HF samples. This corresponds to the highest free SiO_2 content because of the decomposition by acid attack, since a part of octahedral sheets was dissolved by the acid treatment (Yildiz et al., 2004). Table 4.2 shows the characteristic FTIR bands of the untreated and acid activated clays.

Table 4.2: Characteristics FTIR bands of the untreated and acid activated clays.

Absorbance (cm^{-1})	**Band assignment**
3622, 3408	O-H stretching
1637	Hydration OH
1057	Si-O stretching
914	OH deformation, linked to $2Al^{3+}$
878	OH deformation, linked to Al^{3+} and Mg^{2}
796	Silica phase
694	OH deformation, linked to Mg^{2+}
520	Si-O deformation and Al-O stretching

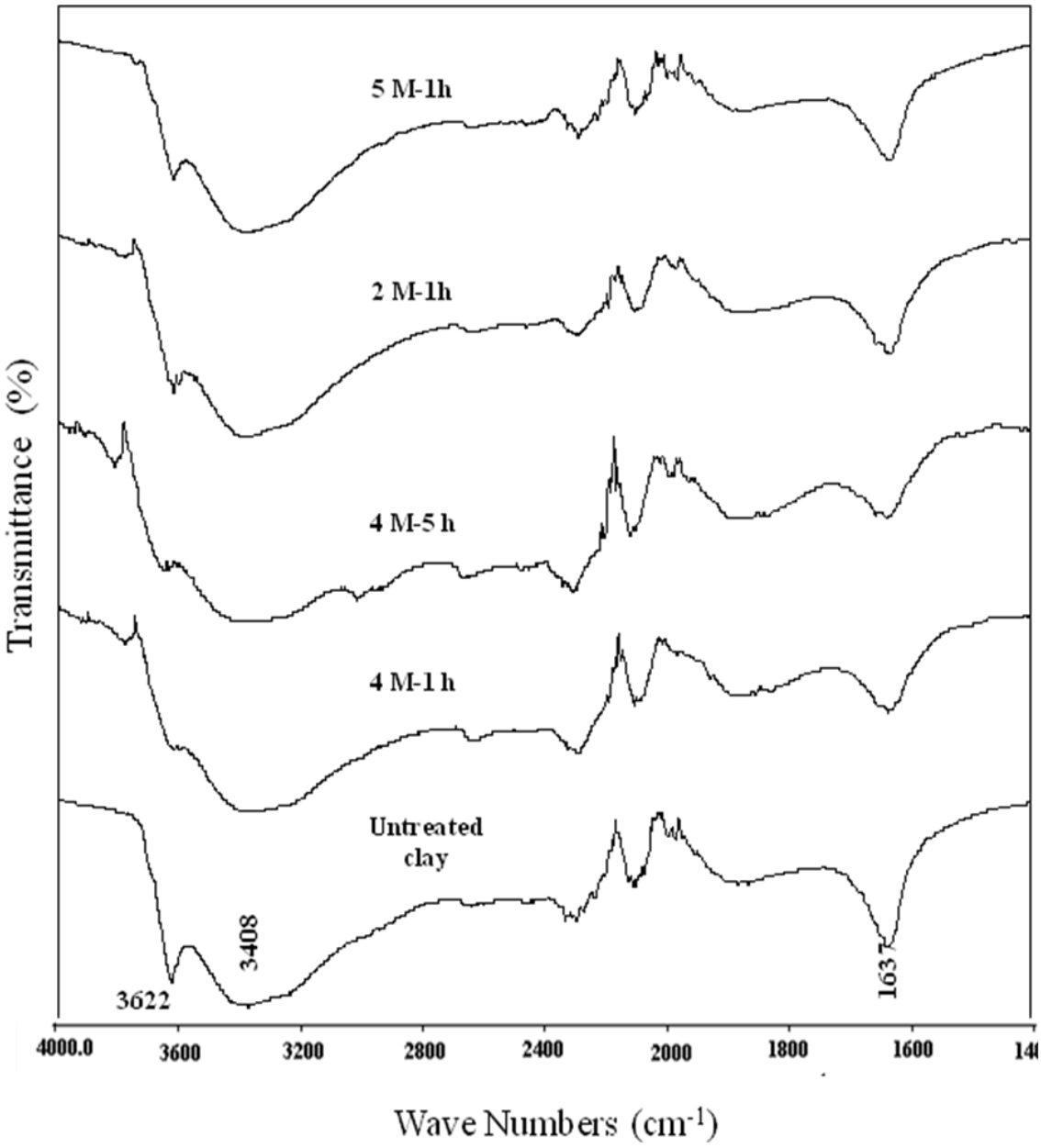


Figure 4.5: FTIR Spectra of the untreated clay and H_2SO_4 activated clays at (4000-1400 cm^{-1}).

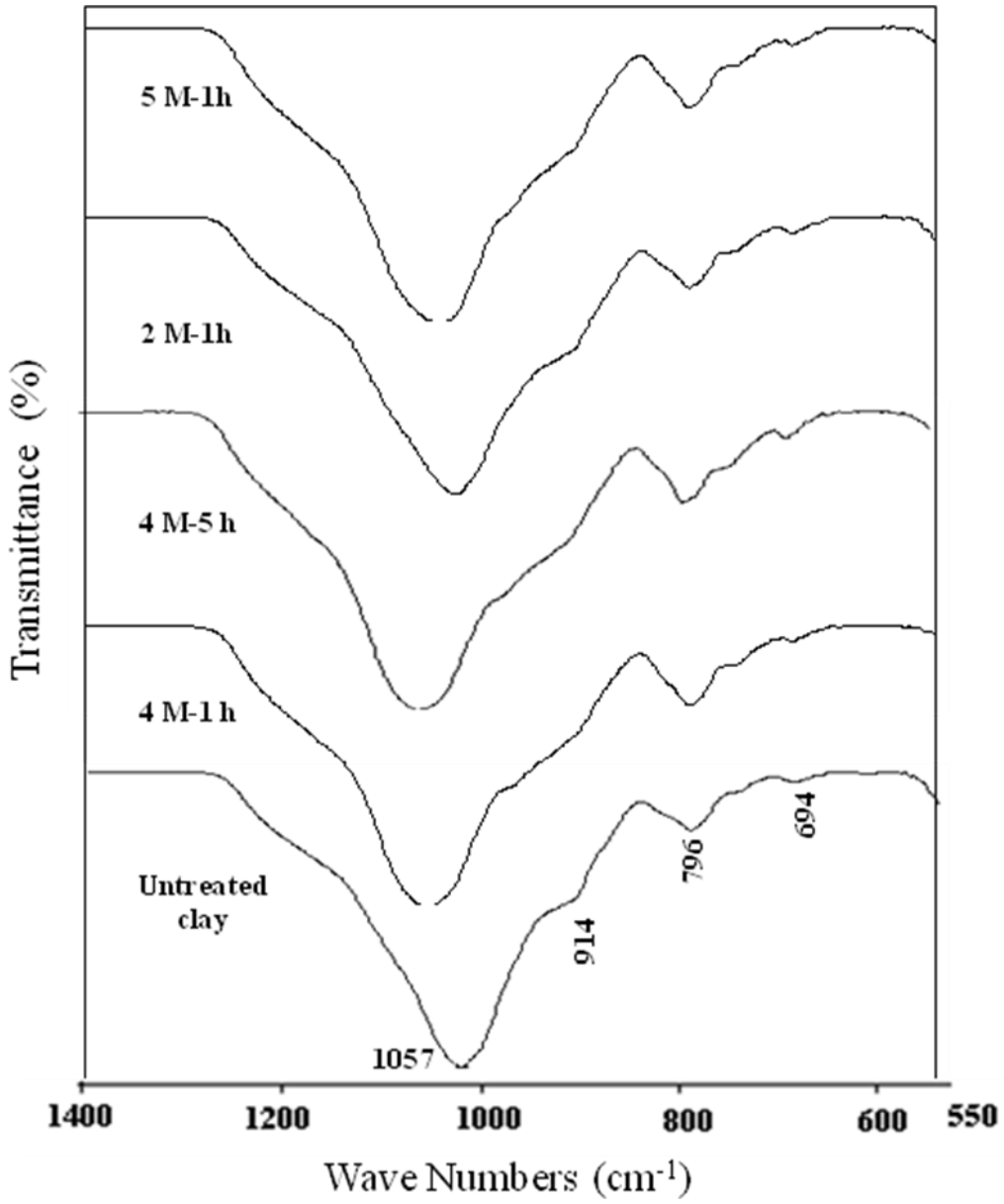


Figure 4.6: FTIR Spectra of the untreated clay and H_2SO_4 activated clays at (1400-550 cm^1).

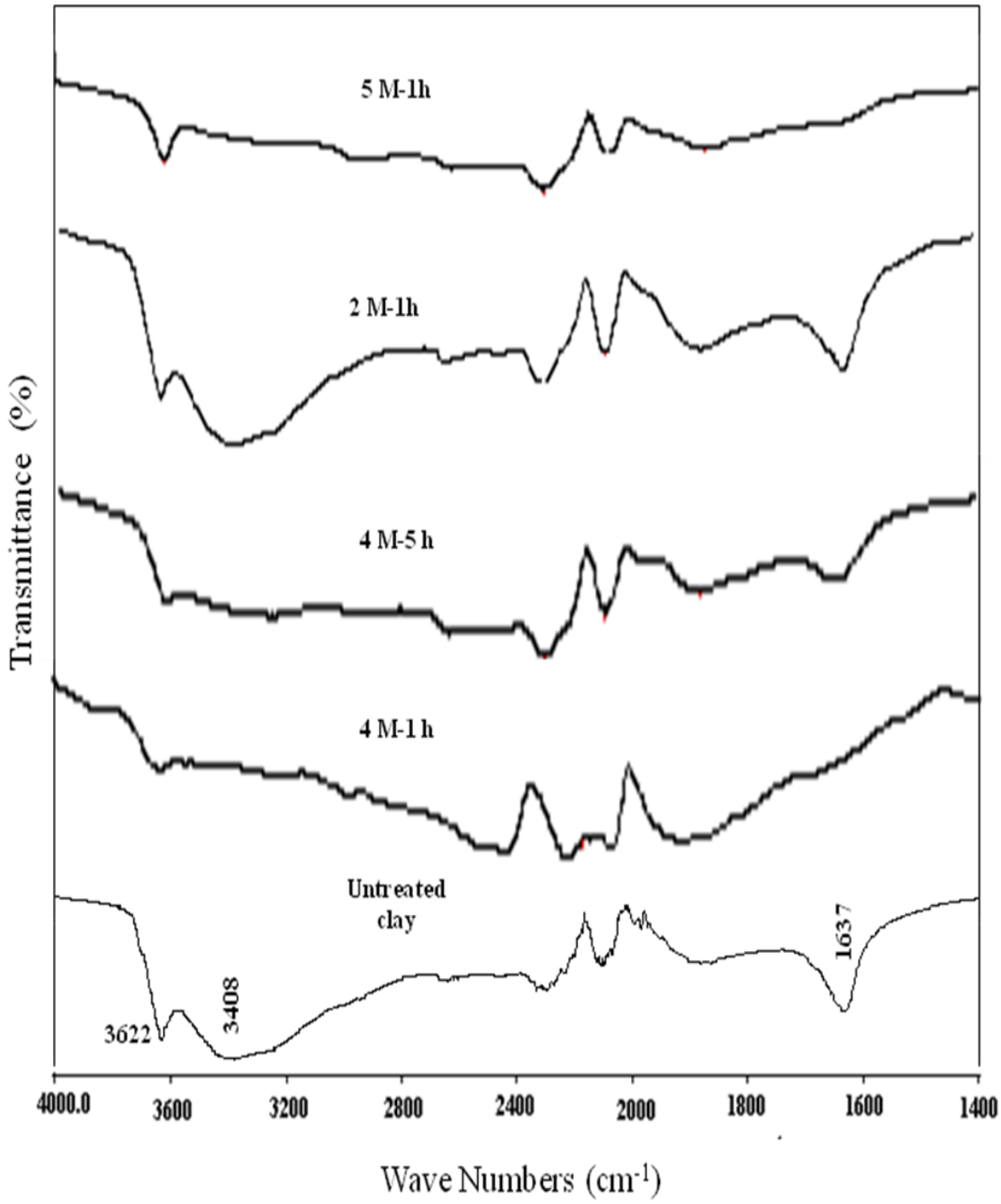


Figure 4.7: FTIR Spectra of the untreated clay and HF activated clays at (4000-1400 cm^{-1}).

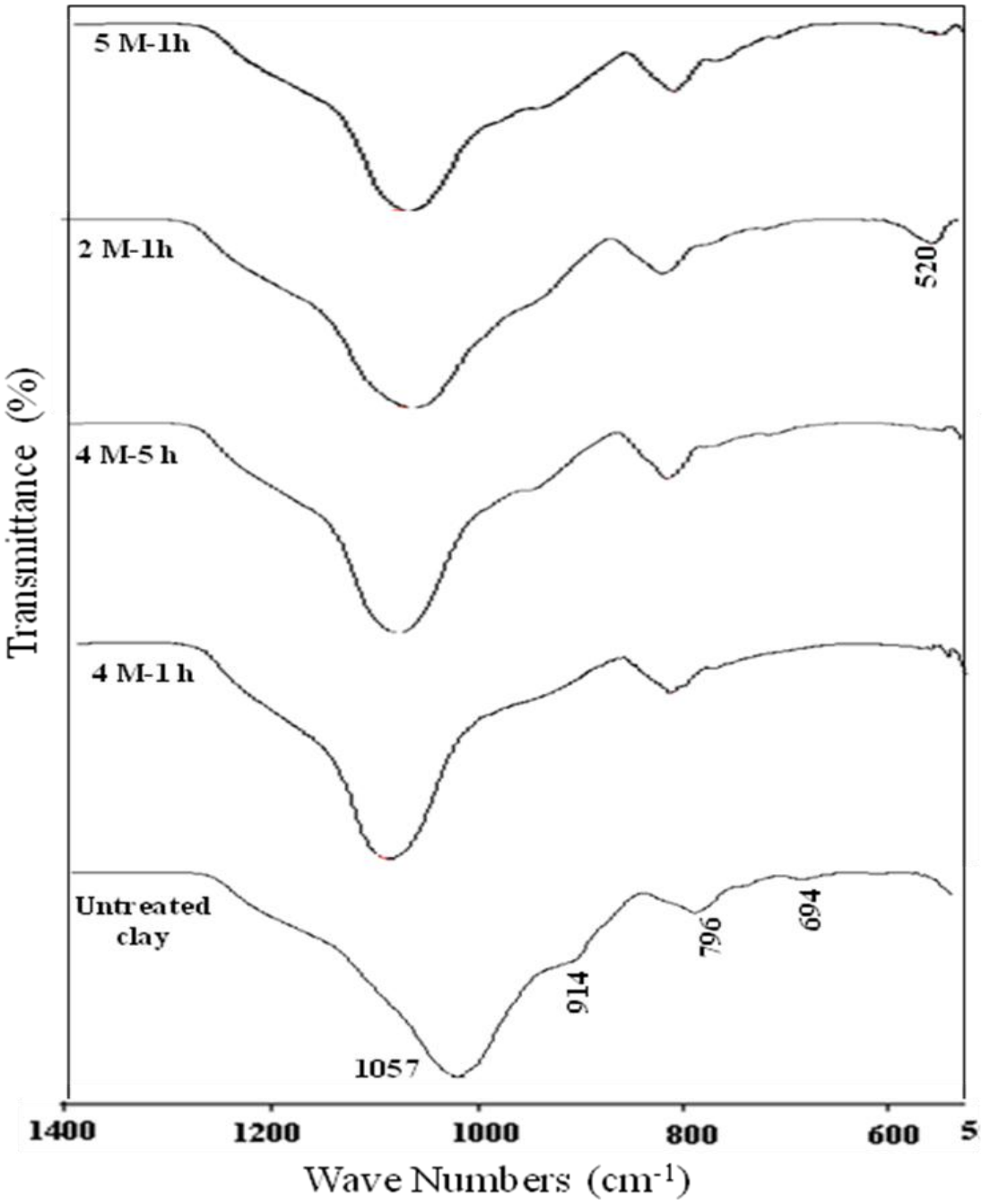


Figure 4.8: FTIR Spectra of the untreated clay and HF activated clays at (1400-500 cm^{-1}).

4.1.5 BET Surface Area

The specific surface area of the natural and acid activated clay samples are given in Tables 4.3 and 4.4. The acid activation process resulted in an increase in the value of surface area from 43.05 to 254.80 m^2 g^{-1} and a further increase in total pore volume from 0.14 to 0.64 cm^3 g^{-1} for H_2SO_4 activated clay. Similarly, the surface area was increased up to 70.11 m^2 g^{-1} and total pore volume increased from 0.14 to 0.31 cm^3 g^{-1} after treatment with HF. These results are in good agreement with the work done by Valenzuela-Diaz and Souza-Santos, (2001) which reported that after the acid treatment, acid activated clay shows comparatively much higher activity and the specific surface area is higher than that of the natural clay.

From Tables 4.3 and 4.4, it can be seen that HF activated clays have low surface area but very high average pore diameters compared to clays activated with H_2SO_4. The highest surface area for clay activated with HF was obtained at 3 M HF. Although 3 M HF activated clay had low surface area, it was found to have the capability to remove the colour from CPO. This result is in agreement with the study conducted by Kiš et al., (2002) in which the bleaching capacity of the samples was determined by the average pore diameter and did not only depend on the specific surface area. This observation was also reported by Welsh & Bogdanor, (1993) who found that high average pore diameter and total pore volume result in high bleaching capacity for the adsorption of phospholipid and soaps from the oil. It is evident that the modification of the textural properties is related to the changes in the montmorillonite structure which occurred during acid treatment. Therefore, it is important to monitor the structural and textural modification of montmorillonite occurring during the treatment (Kheok & Lim, 1982).

Table 4.3: Textural properties of the activated sulphuric acid under different conditions

Samples	Surface area (m^2g^{-1})	Total pore volume (c^3g^{-1})	Average pore diameter (nm)
Natural	43.05	0.1393	60.00
(2M-1h)	201.90	0.2998	59.40
(2M-3h)	105.00	0.2010	85.10
(2M-5h)	112.90	0.2129	75.47
(2M-7h)	98.05	0.2050	70.10
(3M-1h)	163.70	0.2705	66.11
(3M-3h)	254.00	0.4262	64.58
(3M-5h)	322.60	0.7598	94.20
(3M-7h)	281.50	0.6362	85.01
(4M-1h)	216.90	0.3834	70.71
(4M-3h)	189.20	0.3514	74.28
(4M-5h)	98.21	0.2252	91.73
(4M-7h)	90.15	0.2122	85.01
(5M-1h)	176.80	0.3709	83.90
(5M-3h)	254.80	0.6402	100.50
(5M-5h)	155.30	0.4423	94.00
(5M-7h)	140.01	0.3501	91.05
(6M-1h)	169.60	0.4276	100.90
(6M-3h)	115.05	0.3015	98.10
(6M-5h)	105.50	0.2815	96.50
(6M-7h)	90.05	0.2025	86.20

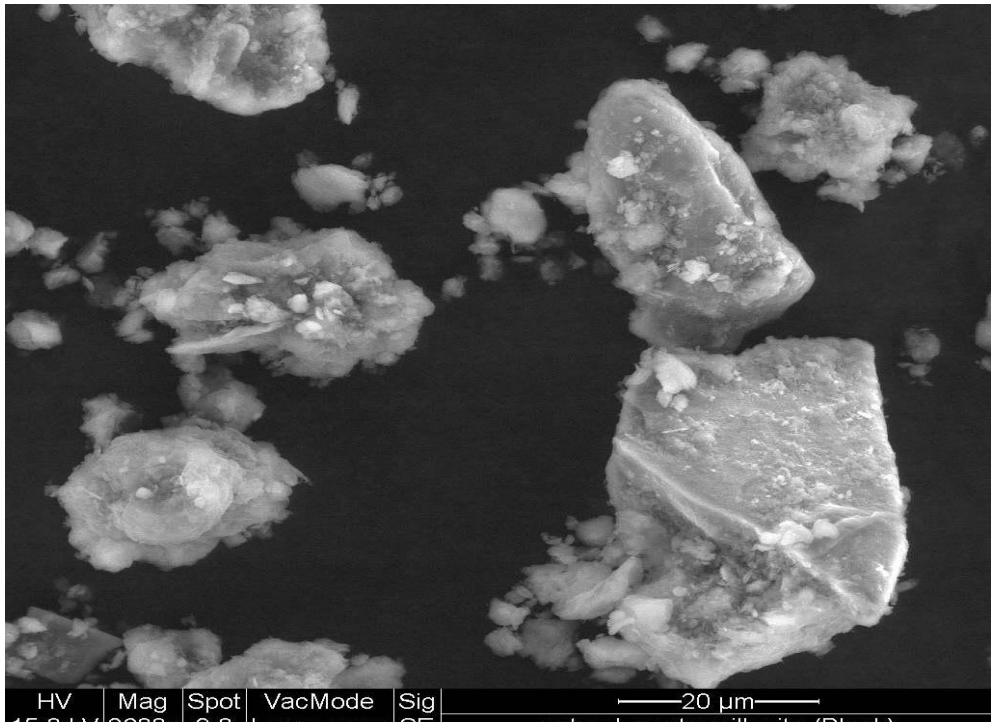
Table 4.4: Textural properties of the activated hydrofluoric acid under different conditions

Samples	Surface area (m^2g^{-1})	Total pore volume (c^3g^{-1})	Average pore diameter (nm)
Natural	43.05	0.1393	60.00
(2M-1h)	45.00	0.1805	129.40
(2M-3h)	35.05	0.1303	105.01
(2M-5h)	31.40	0.1274	111.05
(2M-7h)	30.05	0.1252	162.30
(3M-1h)	70.11	0.3129	209.00
(3M-3h)	32.39	0.1692	105.01
(3M-5h)	21.55	0.0987	181.80
(3M-7h)	28.05	0.1501	151.05
(4M-1h)	32.39	0.1692	178.50
(4M-3h)	33.58	0.1163	138.50
(4M-5h)	26.28	0.0962	146.40
(4M-7h)	23.01	0.0801	125.05
(5M-1h)	24.64	0.0928	150.70
(5M-3h)	16.89	0.0471	111.50
(5M-5h)	18.62	0.0588	126.30
(5M-7h)	15.01	0.0501	121.05
(6M-1h)	16.62	0.0779	115.05
(6M-3h)	18.65	0.0881	120.15
(6M-5h)	20.01	0.0951	118.15
(6M-7h)	19.05	0.0901	108.20

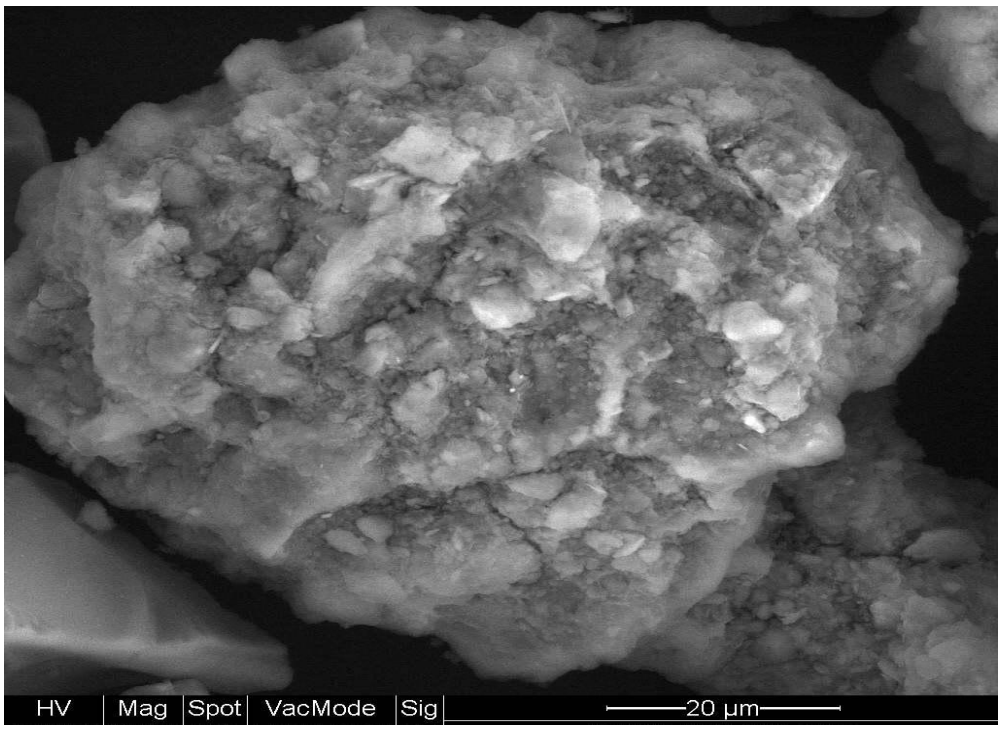
4.1.6 Scanning Electron Microscope (SEM)

SEM was used to investigate the changes in morphological features of the natural and acid activated clay samples. Figure 4.9 shows the SEM micrographs of the natural and acid activated clays at 2 M 1 h and 6 M 1 h. The surface morphology of the natural clay is different from that of the acid activated clays. Natural clay consists of thick but small agglomerates of montmorillonite with irregular shapes and partly sharp grain boundaries. This is due to their small particle size and the specific surface area which ranged between 16 and 97 m^2g^{-1}. This is in agreement with Steudel et al., (2009) who reported that all natural clays consist of thick agglomerates of montmorillonite with irregular shapes and partly sharp grain boundaries. As observed from Figure 4.9 (b), (c), (d) and (e), the morphologies of the structures showed remarkable changes after acid treatment. The particles of the treated montmorillonite clay are smaller and thinner compared to those of the natural clay. However, they are still agglomerated.

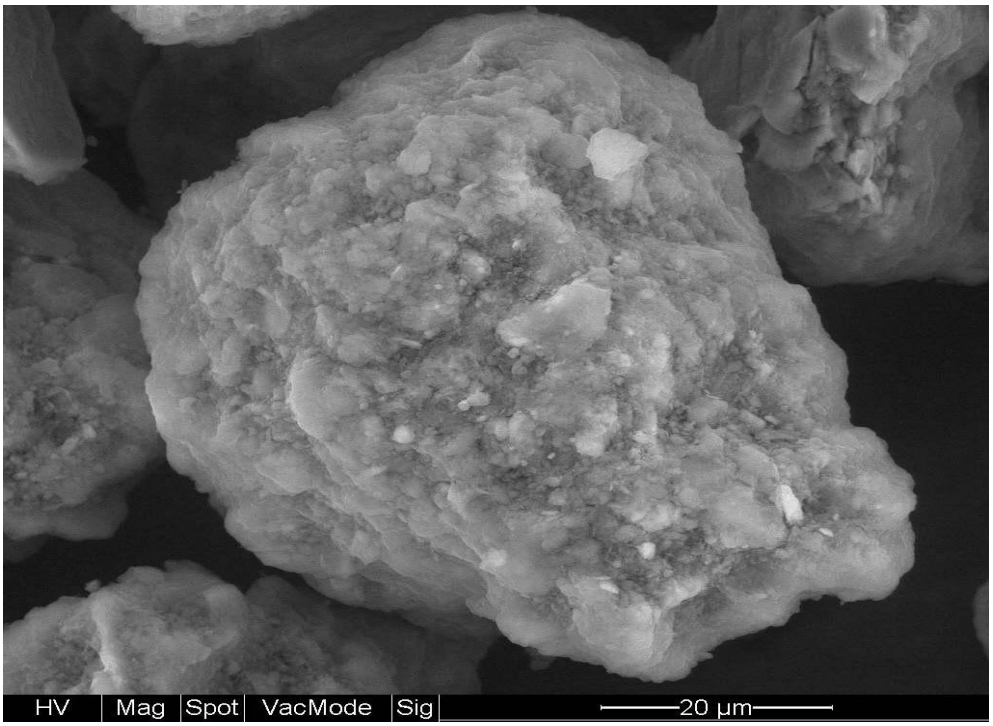
a)



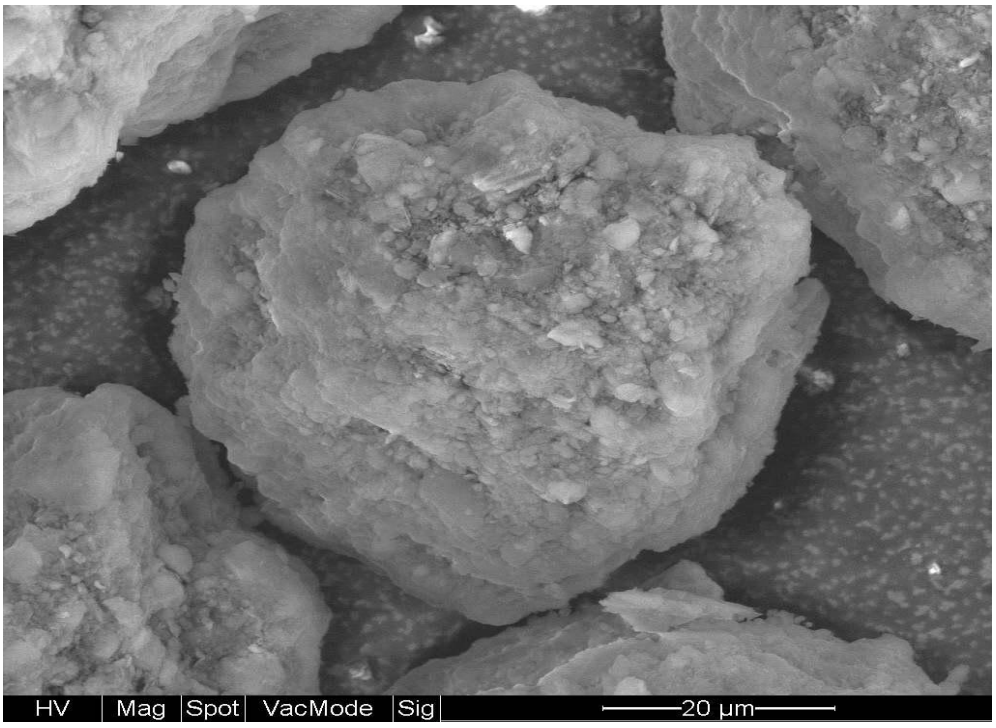
b)



c)



d)



e)

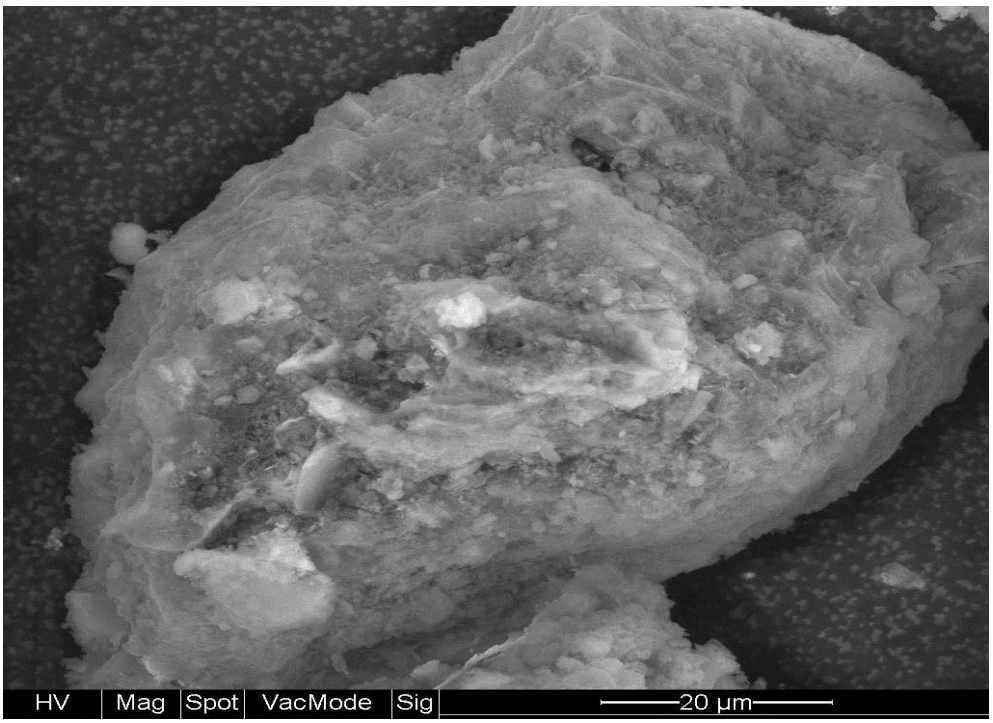


Figure 4.9: Scanning electron micrographs of a) natural clay, b) activated clay with H_2SO_4 at (2M 1h), c) activated clay with H_2SO_4 at (6M 1h), d) activated clay with HF at (2M 1 h) and e) activated clay with HF at (6M 1 h).

4.2 Part 2: Bleaching performance of acid activated clays.

In order to find the most appropriate conditions for the clay activation, the effects of the type of acid, acid concentration and activation time on Lovibond colour removal in the bleaching process was investigated throughout a series of experiments. The best conditions were selected and used to investigate the performance of H_2SO_4 and HF activated clays in removing the other undesirable compounds in the palm oil such as free fatty acid, peroxide value and phosphorus content. The results are compared with those of the natural clay and commercial activated clay. During the experiments, each sample was run in duplicates and the analysis of oil characteristics were carried out in triplicates in order to get good average results.

4.2.1 Characteristics of crude palm oil

Table 4.5 illustrates the characteristics of the CPO which was used in this study. It was found that the free fatty acid, peroxide value, phosphorus, colour and carotene content were within the range of the standard-quality CPO. Therefore, it is important to monitor the quality of the CPO before and after the bleaching process, in order to obtain the most effective bleaching process without affecting the later stage of the refining process.

Table 4.5: Physicochemical characteristics of the crude palm oil used in the study and its standard specifications

Constituent	Specifications for Standard-Quality CPO	CPO (This study)
Free Fatty Acid (%)	2.0-5.0	3.40
Peroxide Value ($meqkg^{-1}$)	1.5-5.0	2.05
Phosphorus (ppm)	10-20	12.34
Lovibond Colour, 1″ cell	Orange Red	45.5
Carotene (ppm)	500-700	545

4.2.2 Colour removal efficiencies of activated clays

Colour is an important factor in the analysis of the quality of bleached palm oil (Low et al., 1998). Dark coloured oil requires higher processing cost to be converted into an acceptable light-coloured product since the dark colour may affect the quality of the finished oil product (Ahmad et al., 2009). The colour level of the bleached palm oil was used to monitor the reaction as it is a good indicator for determining the quality of bleached palm oil.

4.2.3 Activation with H_2SO_4

4.2.3.1 Effect of acid concentrations

Acid concentration is one of the most important factors affecting the performance of acid activated clay. The effect of acid concentrations on colour removal of the bleached palm oil was investigated by varying the acid concentrations from 2 to 6 Molar. Table 4.6 shows the results of the colour measurements, according to the Lovibond (R,Y) after bleaching palm oil with H_2SO_4 activated clay.

The colour of the crude palm oil was (45.5±0.5R, 4.5±0.25Y). A significant change in the colour of the oil was seen upon increasing H_2SO_4 concentration during activation beyond 3 M. For instance, a significant colour reduction was observed in the clay activated with 5 M H_2SO_4. Based on the results, it was clear that the highest colour removal was attained after activation with 5 M H_2SO_4 (24.4±0.75R, 2.4±0.40Y). Meanwhile, the highest colour removal percentage which was calculated by equation 3.3 using red colour index of the bleached palm oil as 46.37% (Figure 4.10). On the other hand, by increasing acid concentration to 6 M, the percentage of colour removal of the bleached palm oil decreased significantly (Figure 4.10). This may be due to the excessive leaching of the octahedral cations during acid activation, which is attributed to the collapse of the clay mineral structure. Consequently, the specific surface area is decreased causing a reduction in the ability of the adsorbent to remove the red colour in the oil (Didi et al., 2009; Hussin et al., 2011).

Results indicated that acid concentration had the most significant ($p<0.001$) effect on colour removal efficiency (Table 4.7). In contrast, its interaction effect and activation time show the least considerable ($p<0.001$) effect on colour removal. Besides, the removal of colour in the bleached palm oil is highly dependent on the acid concentration used for clay activation. Therefore, it can be concluded that 5 M H_2SO_4 is an appropriate concentration for colour removal from the oil.

Table 4.6: Colour measurement in Lovibond (R,Y) units of H_2SO_4 activated clays.

Activation time: 1 h

Acid Concentration (M)	Lovibond Red Index, R	Lovibond Yellow Index, Y
2	26.5±0.25	2.9±0.12
3	26.5±0.25	2.9±0.17
4	30.3±0.29	3.1±0.36
5	24.4±0.75	2.4±0.40
6	38.3±0.29	3.5±0.25

The values are expressed as means ± SD of triplicate analysis

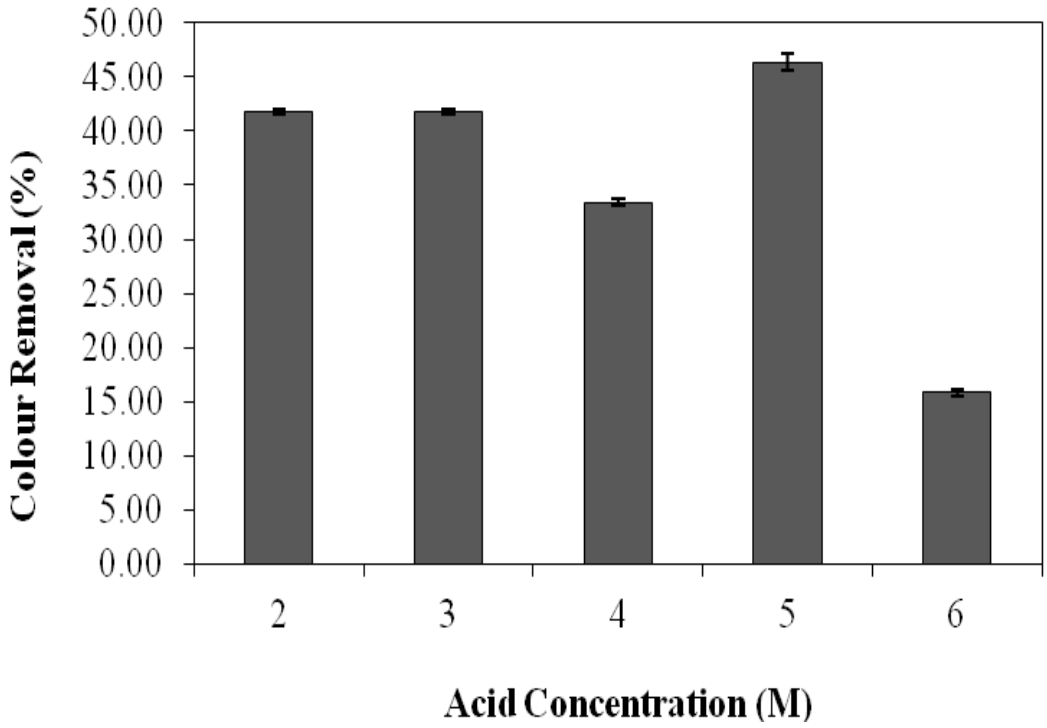


Figure 4.10: Effect of H_2SO_4 concentration on the percentage of Lovibond red colour removal at 1 hour activation time

Table 4.7: The significance of each independent variable effect shown by the F-ratio and p-value

Independent variables		
	F-value	**P-value**
Acid Concentration	4028.25	0.000*
Activation Time	2233.59	0.000*
Interaction	559.83	0.000*

*Significant ($p < 0.001$)

4.2.3.2 Effect of activation times

The effect of activation time on the colour removal is shown in Figure 4.11. It is clear that an increase in the activation time leads to a decrease in the amount of colour removed. These results are in concordance with those obtained by Lin & Lin (2005), who showed that the colour of oil increases proportionally with the increase in the activation time. As shown in Table 4.8, when the activation time was increased from 1 to 7 hours, the Lovibond colour of the oil obtained for the activation with H_2SO_4 increased from 24.4±0.75 to 29.8±0.56. This was due to the significant changes in the chemical composition and disintegration of the clay mineral structure which were observed in the clay minerals.

The results demonstrated that activation times longer than 5 hours are not recommended because with longer times, oil colour level of 29.8±0.56 could be obtained and the cost of operation needed would be higher. Therefore, in order to save energy and to reduce the cost of pretreatment process, activation time of 1 hour is considered sufficient to attain the highest removal of colour from the oil of up to 46.37% (Figure 4.11).

Table 4.8: Colour measurement in Lovibond (R,Y) units of H_2SO_4 activated clays.

Acid concentration: 5 M

Activation Times (h)	Lovibond Red Index, R	Lovibond Yellow Index, Y
1	24.4±0.75	2.4±0.40
3	27.5±0.53	3.0±0.29
5	29.8±0.56	3.1±0.25
7	29.8±0.56	3.1±0.25

The values are expressed as means ± SD of triplicate analysis

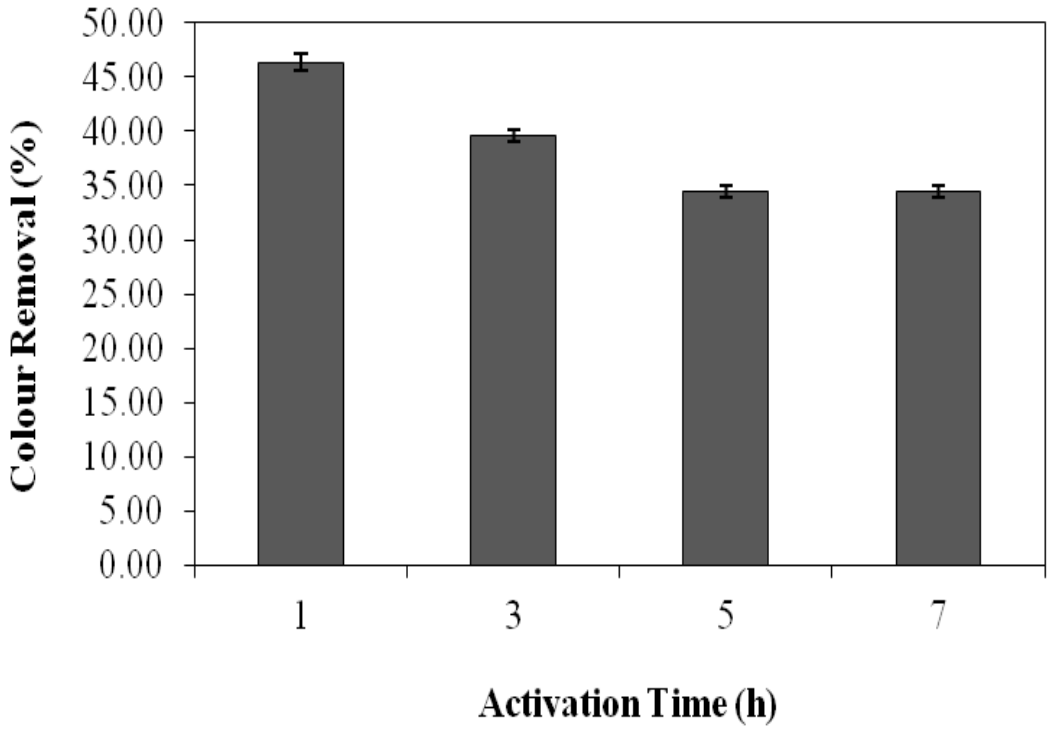


Figure 4.11: Effect of H_2SO_4 activation times on the percentage of Lovibond red colour removal at 5 M of acid concentration.

4.2.4 Activation with HF

4.2.4.1 Effect of acid concentrations

Figure 4.12 shows the results of the colour removal after bleaching of palm oil with HF activated clays. In this experiment, the performance of HF activated clays in removing the colour pigment from the oil was compared with H_2SO_4 activated clays.

The highest colour removal for HF activated clay (45.05%) was observed after activation with 3 M HF, with the corresponding lovibond colour index of (25.0±0.40R, 2.5±0.25Y) (Table 4.9). However, the data in Figure 4.12 for activation with 3 M HF suggests that colour removal efficiency is directly and solely related to the average pore diameter. Nevertheless, it is inversely related to the specific surface area. This result is entirely different from what has been stated about activation with H_2SO_4. When the pore diameter was larger than 100 nm; average pore diameter controlled the bleaching efficiency. This is due to the fact that molecules of colour pigments and impurities are too large to diffuse through the pore and thus are not adsorbed on the surface of the pore which is relatively small. This observation was further supported by a research conducted by Chang, (2001) where the increase in colour removal efficiency was due to the increase in the average pore diameter and not the specific surface area.

Results indicate that, the clay activated with 3 M HF, which is considered a medium activation clay is sufficient to give the highest removal of colour from CPO, however, in the activation with H_2SO_4 the highest colour removal is achieved after treatment with a higher acid concentration of 5 M. It is clearly demonstrated that there is no significant difference in the percentage of colour removal between the clay activated with 5 M H_2SO_4 and those that are activated with 3 M HF. It observed from Table 4.10, that colour removal is significantly ($p < 0.001$) affected by all the independent variables. The results indicate that acid concentration has the least significant ($p < 0.001$) effect on

colour removal, while its interaction and activation time have the most considerable ($p < 0.001$) effect on colour removal.

Table 4.9: Colour measurement in Lovibond (R,Y) units of HF activated clays.

Activation time: 1 h

Acid Concentration (M)	Lovibond Red Index, R	Lovibond Yellow Index, Y
2	38.7±0.17	3.7±0.29
3	25.0±0.40	2.5±0.25
4	40.2±0.36	3.8±0.25
5	43.3±0.15	4.0±0.25
6	29.6±0.17	3.1±0.17

The values are expressed as means ± SD of triplicate analysis

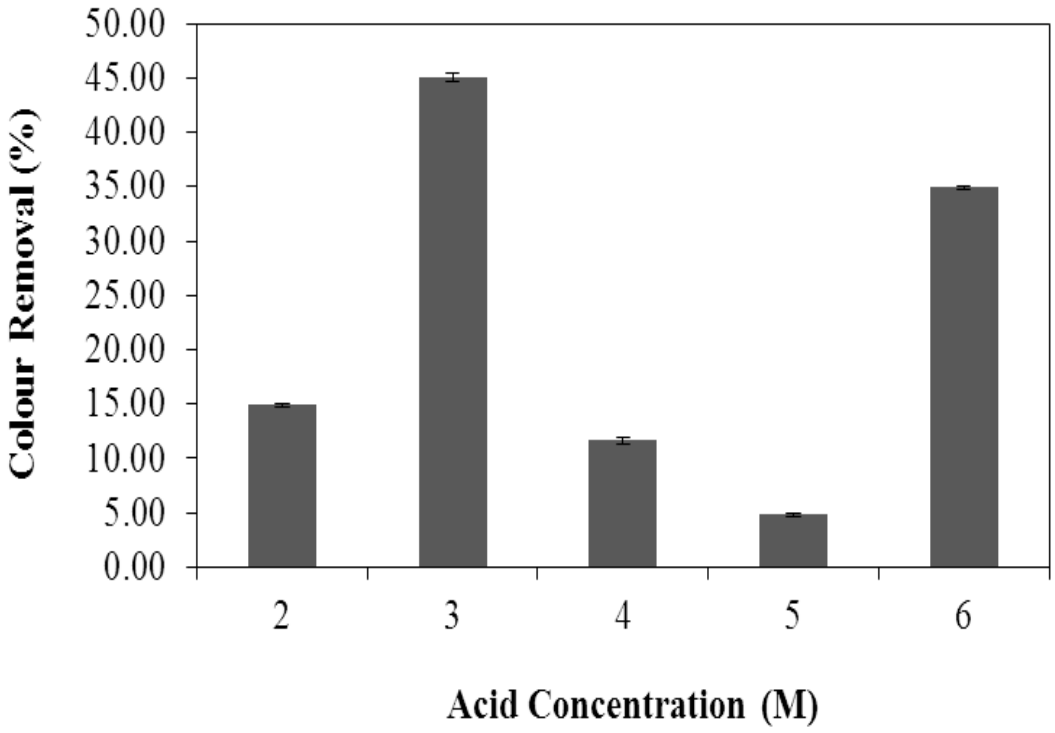


Figure 4.12: Effect of HF concentration on the percentage of Lovibond red colour removal at 1 hour activation time.

Table 4.10: The significance of each independent variable effect shown by the F-ratio and p-value

Independent variables		
	F-value	**P-value**
Acid Concentration	1047.97	0.000*
Activation Time	5253.21	0.000*
Interaction	1099.80	0.000*

*Significant ($p < 0.001$)

4.2.4.2 Effect of activation times

The effect of activation time was studied in the range from 1 to 7 hours. At these conditions, the highest colour removal was obtained at 1 hour activation time with the corresponding Lovibond colour index of (25.0±0.40R, 2.5±0.25Y) (Table 4.11). As illustrated in Figure 4.13, increasing the activation time to 7 hours resulted in a decrease in the colour removal from the oil. Despite the observation that the 3 M HF activated clay was capable of reducing the colour from the oil; it was found that the activation process took a shorter time to be completed, as shown in Figure 4.13. This observation was similar to what had been stated regarding the activation with H_2SO_4. Therefore, it can be concluded that 1 hour of activation time is an appropriate condition for this purpose.

Based on the results, it was obvious that the colour removal efficiency from the oil decreased dramatically at 7 hours of activation time. The results reveal that, for HF activated clay, 7 hours activation time is found to be ineffective for removing the colour from the oil.

Table 4.11: Colour measurement in Lovibond (R,Y) units of HF activated clays. Acid concentration: 3 M

Activation Times (h)	Lovibond Red Index, R	Lovibond Yellow Index, Y
1	25.0±0.40	2.5±0.25
3	38.5±0.87	3.7±0.12
5	38.7±0.29	3.7±0.17
7	61.5±0.25	6.1±0.17

The values are expressed as means ± SD of triplicate analysis

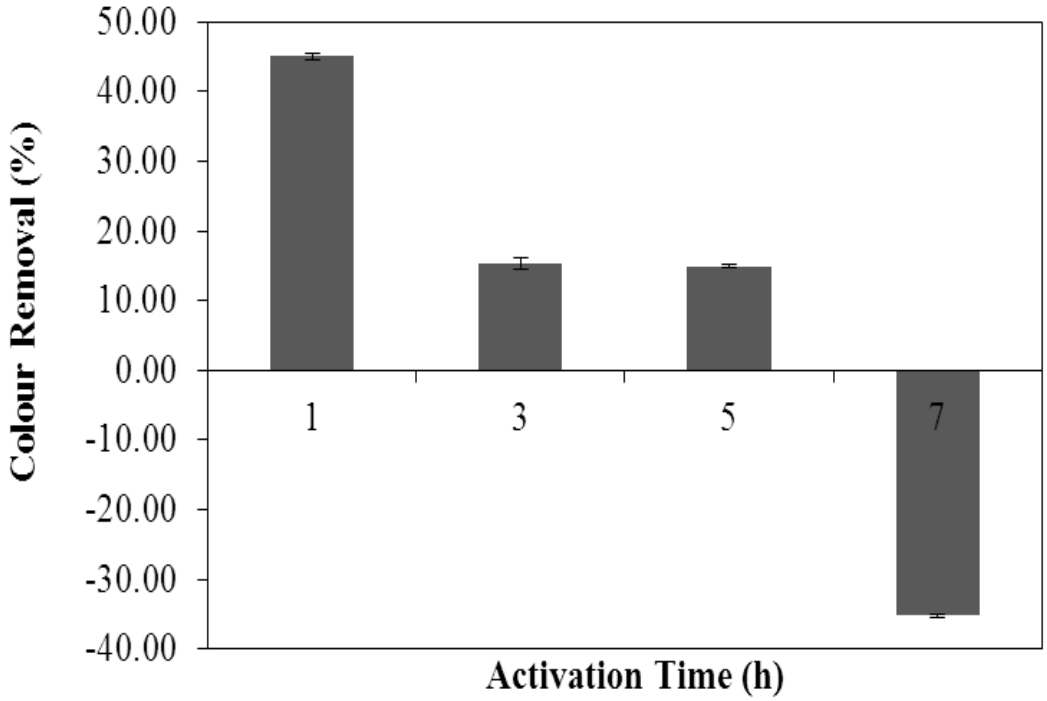


Figure 4.13: Effect of HF activation times on the percentage of Lovibond red colour removal at 3 M of acid concentration.

4.2.5 Comparison under identical conditions

The colour removal efficiency of the clay activated with H_2SO_4 and HF obtained in this study was compared with the natural clay and commercial activated clay, as presented in Table 4.12. The results in Table 4.12 show that clays activated with 5 M H_2SO_4 and 3 M HF solutions are found to be effective adsorbents for the removal of the colour pigment from the oil. Moreover, all acid activated clays are not significantly different. It is clear that, the highest red colour removal of the adsobents can be ranked in the order of: 5 M H_2SO_4 (46.37%), 3 M HF (45.05%), commercial activated clay (42.89%) and natural clay (34.07%).

Table 4.12: Effect of different types of adsorbents on the percentage of red colour removal in the bleached palm oil

Adsorbents	Red Colour Removal (%)
Natural clay	34.07
Commercial activated clay	42.89
5 M H_2SO_4 at 1 hour	46.37
3 M HF at 1 hour	45.05

The results obtained in this study were also compared with the results established in the literature. For HF activated clay, no other studies on this type of acid activated clay was found, therefore a comparison was made with other types of acid in terms of the effectiveness of colour pigment removal in the oil (Table 4.13). As reported by Usman et al., (2012), increasing acid concentration, increased the colour removal significantly. They showed that 3 M of HCl activated clay is an effective adsorbent in removing the colour from the CPO. Their results revealed that the highest colour removal was found to be at 27.27%, which was much lower than that observed in this study, which was

(~46%). Furthermore, Al-Zahrani (1995) has compared the potential of HCl and H_2SO_4 activated clay as adsorbents in the purification of oil. They obtained 43 % removal efficiency through clay activated with 4 M HCl. Meanwhile, for H_2SO_4 activated clay, the highest colour removal was achieved at 11.5 M which corresponds to 40% colour removal. The results indicated that higher colour removal can be achieved at higher acid concentrations. However, in this study, for H_2SO_4 activated clay, lower acid concentration was found to be sufficient to obtain the highest colour removal from the oil.

From the data in Table 4.13, it can be concluded that clays activated with 5 M H_2SO_4 and 3 M HF solution at 1 hour activation time were the most effective adsorbents for removing the colour in the oil compared to other adsorbents mentioned in the literature. Therefore, the above treatment was selected and used for further studies.

Table 4.13: Effect of different types of adsorbents on the percentage of colour removal in the bleached palm oil

Type of acid activated clays	Optimum Acid Concentration (M)	Lovibond colour (Y,R) index	Colour Removal (%)	References
HCl	3	27.5	27.27	(Usman et al., 2012)
Commercial activated clay	-	28.5	-	(De et al., 2009)
Commercial activated clay (H_2SO_4)	-	-	32.13	(Omar et al., 2003)
H_2SO_4	11.5	-	40.00	(Al-Zahrani, 1995)
HCl	4	-	43.00	(Al-Zahrani, 1995)
HF	3	25.0	45.05	This study
H_2SO_4	5	24.4	46.37	This study

4.2.6 Carotene content of bleached palm oil

As shown in Table 4.5, the crude palm oil contains 545 ppm of β-carotene. The results indicate that, a decrease in the Lovibond colour caused a decrease in the β-carotene content of the oil when the clay used was activated with H_2SO_4. The significant decrease in β-carotene content after bleaching with H_2SO_4 activated clay is clearly shown in Figure 4.14. It was observed that, the lowest β-carotene content was obtained after treatment with 5 M H_2SO_4 activated clay. The reasons behind this finding are

related to the changes in the textural properties of the clay minerals. Based on this observation, it can be concluded that the improved ability of the adsorbent to adsorb the carotene from the CPO was due to its high adsorption capacity and its affinity towards carotene (Espantaleón et al., 2003).

On the other hand, there was a slight decrease in the β-carotene content when the palm oil was bleached with HF activated clay. The results for HF activated clay did not agree with those of Gonçalves et al., (2007), who reported that the β-carotene content would be reduced to half its original value after the bleaching process, and these components will be completely destroyed during the deodorization stage. A similar observation has been made by Lin et al., (2009), where they reported that acid activated clay reduced substantial amounts (up to 94%) of β-carotene content from the oil after the bleaching process.

However, it is interesting to note that, the treated palm oil using 3 M HF activated clay had the ability to retain more than 96 % of the original β-carotene content, from 545 ppm in the CPO to 523 ppm in the bleached palm oil (Table 4.14). While natural clay, commercial activated clay and 5 M H_2SO_4 activated clay retain only 58.90 %, 77.06% and 73.03 % of the original β-carotene content, respectively. Thus, these results indicate that 3 M HF activated clay produced bleached oils with a higher β-carotene content as well as substantial colour reduction. Therefore, it can be concluded that, 3 M HF had the ability to prevent β-carotene losses from the oil. This study also demonstrated other advantages of using 3 M HF activated clays as adsorbents in the purification of the CPO.

Table 4.14: Effect of different types of adsorbents on the β-carotene content of bleached palm oil

Types of adsorbent	β-carotene content (ppm)
Natural clay	321±9.08
Commercial activated clay	420±7.07
Activated clay with 5 M H_2SO_4	398±4.50
Activated with 3 M HF	523±5.80

The values are expressed as means ± SD of triplicate analysis

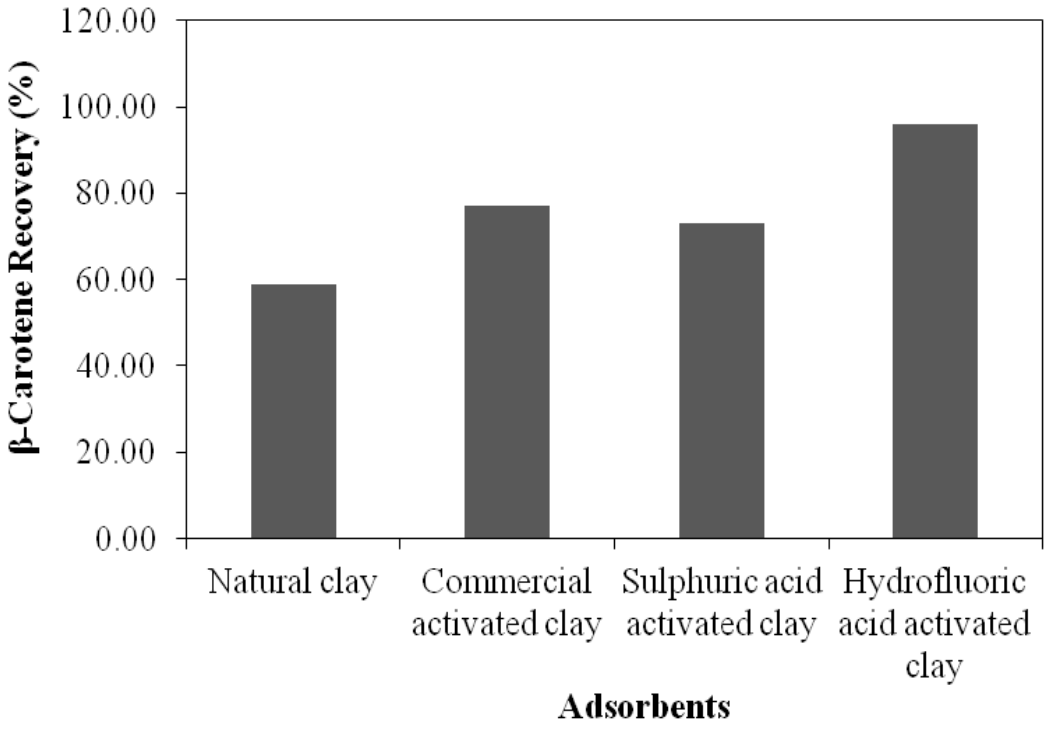


Figure 4.14: Effect of different types of adsorbent on the percentage of β-carotene recovery

4.2.7 Phosphorus content of bleached palm oil

Phosphorus content in palm oil is considered as an undesirable impurity causing refining problems, oil losses and higher production cost (Szydłowska-Czerniak & Szłyk, 2003). The effects of different types of adsorbents on the phosphorus content of bleached palm oil are shown in Table 4.15. It is evident that clays activated with 5 M H_2SO_4, 3 M HF at 1 hour and commercial activated clay were found to be effective adsorbents for the removal of the phosphorus content. Whereas, the natural clay was found to be ineffective for phosphorus content removal from bleached palm oil. A similar observation was reported by Wei et al., (2004) and Lin et al., (2009), who showed that acid-activated clay effectively contributed to the removal of the phosphorus content. In addition, Kheok & Lim, (1982) explained that the mechanism for phosphorus reduction was due to the adsorption of the phosphorus ions on the lattice structure of the clay.

According to Zufarov et al., (2008), degumming and bleaching treatments play a vital role in the physical refining of palm oils. However, these treatments cannot guarantee the achievement of low phosphorus contents required for physical refining, and were not always optimally suited for all types of oil quality because of the high content of non-hydratable phospholipid (NHPL). In this study physical refining was chosen as the treatment for the degumming and bleaching processes, which indicates that the factor mentioned above would significantly affect the phosphorus content. As reported by Rossi et al., (2003), degumming tends to increase the levels of phosphorus. This increase was probably caused by the ions brought into the oil from the phosphoric acid, which was used as the degumming media. In this study, the trend by which the phosphorus content decreased was in contrast with the results of Rossi et al., (2003). This observation was also reported by Thomopoulos & Zhia (1993), who stated that the

phosphorus removal efficiency was dependent on the type of acid and the quality of the oil used.

Table 4.15: Effect of different types of adsorbents on the phosphorus content of bleached palm oil

Adsorbents	Phosphorus content (ppm)
Natural clay	12.93±0.12
Commercial activated clay	6.20±0.29
Activated clay 5M H_2SO_4	6.13±0.25
Activated with 3M HF	6.17±0.08

The values are expressed as means ± SD of triplicate analysis

4.2.8 Free Fatty acid of bleached palm oil

The level of free fatty acids (FFA) is a good indicator, which is commonly used in the oil refinery industry for determining the quality of palm oil during oil production, storage and marketing. The higher the level of the FFA, the poorer the oil quality, therefore the FFA is one of the major components that needs to be eliminated from the crude palm oil in the refining process (Smouse, 1995). The effects of acid activated clays on the FFA content of bleached palm oil are shown in Table 4.16. Based on the results, it was clear that the removal of the FFA content in the oil for the natural clay, commercial activated clay, H_2SO_4 and HF activated clays are not significantly different. The efficiency of the adsorbents in reducing the FFA content can be ranked in the order of: 3 M HF activated clay (2.50±0.030%), 5 M H_2SO_4 activated clay (2.57±0.040%), commercial activated clay (2.65±0.010%) and natural clay (2.68±0.030%).

The results obtained in this study are also compared with the published results in the literature (Table 4.17). As reported by Nguetnkam et al., (2008), clay activated with 8 M H_2SO_4 showed higher reduction in the FFA content of bleached palm oil. This effect was also reported by Huang & Sathivel (2010), where the initial FFA content of the crude oil was 3.5 % and decreased to 3.38 % after treatment with commercial activated clay. However, the results contradict those reported by Wei et al., (2004) which showed that the FFA content of H_2SO_4 activated clay increased to 3.5% after acid activation. A similar observation was made by Usman et al., (2012), where the FFA content increased to 4.71% after treatment with 3 M HCl. Therefore, it can be concluded that clays activated with 3M HF in this study are more effective in removing the FFA content in the oil compared to the commercial activated clay and the other adsorbents reported in the literature. In addition, the favourable operating conditions of lower acid concentration, shorter activation time and higher FFA removal resulting in lower operating cost, have all contributed to promote HF activated clay as a good candidate to be used as an adsorbent in the purification of palm oil.

Table 4.16: Effect of different types of adsorbents on the free fatty acid content of bleached palm oil

Adsorbents	**Free fatty acids content (% FFA)**
Natural clay	2.68±0.030
Commercial activated clay	2.65±0.010
5M H_2SO_4 at 1 hour	2.57±0.040
3M HF at 1 hour	2.50±0.030

The values are expressed as means ± SD of triplicate analysis

Table 4.17: Comparison of HF and H_2SO_4 activated clays with other adsorbents in the removal of FFA content

Type of acids	Optimum acid concentration (M)	Optimum activation time (h)	Free Fatty Acid Content (%)	References
HCl	3	0.5	4.71	Usman et al., (2012)
Commercial activated clay	-	-	3.38	Huang & Sathivel (2010)
H_2SO_4	-	-	3.50	Wei et al., (2004)
H_2SO_4	4	2	12.20	Nguetnkam et al., (2008)
H_2SO_4	5	1	2.57	This study
HF	3	1	2.50	This study

4.2.9 Peroxide value (PV) of bleached palm oil

Peroxide value is considered as one of the most important parameters that measure the oxidative rancidity of palm oil (Wannahari & Nordin, 2012). The initial PV of the crude palm oil used in this study was 2.00 $meqO_2kg^{-1}$. The results obtained in this study highlight the fact that all adsorbents substantially eliminate the PV in the oil to non-detectable value. The high removal efficiency of PV in this study is attributed to the fact that acid activated clays are capable of adsorbing peroxides as well as catalyzing peroxide degradation into secondary oxidation products where these products are removed through bleaching process (Rossi et al., 2003). This finding is further supported by Kheok & Lim, (1982) who stated that, the bleaching process significantly improves the PV of the oil as it practically reaches zero after bleaching.

Similar findings were reported by Wei at al., (2004) stating that the PV was greatly reduced with the acid-activated clay. Therefore, it is believed that acid-activated clays start to prevent the oils from forming hydroperoxides at the early stages of the bleaching process.

4.2.10 Oil retention and Filtration Time

The effects of the percentage of oil retention and filtration time on the bleaching performance of the natural clay, commercial activated clay, H_2SO_4 and HF activated clays, will be discussed in this section.

4.2.10.1 Oil retention

Generally, oil lost to filter cake resulted in oil loss in the bleaching process and it depends on the type of clay used and particle size distribution (Bera et al., 2004; Rich, 1967). Finer particle sizes of clays produce better bleaching results. However, oil retention can be affected adversely. Therefore, minimization of oil retention on filter cake is necessary (Usman et al., 2012). As shown in Table 4.18, the oil retention of natural clay, commercial activated clay, H_2SO_4 and HF activated clays are in the range of 25-37%. Richardson (1978) reported that in the laboratory bleaching processes the retention of oil is around 35%. On the other hand, Bera et al., (2004) reported that in the refinery industries, oil loss varies from 24% to 30%. The results indicated that all of the adsorbents tested were capable of preventing oil losses during the bleaching process, except for the natural clay. It can be seen that 5 M H_2SO_4 and 3 M HF activated clays investigated in this study were found to be effective to minimise the oil loss and hence very economical for the bleaching of palm oil.

Table 4.18: Effect of different types of adsorbent on the oil retention

Adsorbents	Oil retention (%)
Natural clay	37
Commercial activated clay	28
5 M H_2SO_4 at 1 hour	23
3 M HF at 1 hour	25

4.2.10.2 Filtration Time

Generally, the function of the filtration time is to test if the acid activated clay is too smooth or too light, because if the acid activated clay is too smooth or too light, the oil refinery process would take longer time and become ineffective (Usman et al., 2012). Moreover, the cost of operation needed would be higher. Based on the results in Figure 4.15, it was found that all of the acid activated clays tested gave effective results in minimising the filtration rate to less than 2 minutes.

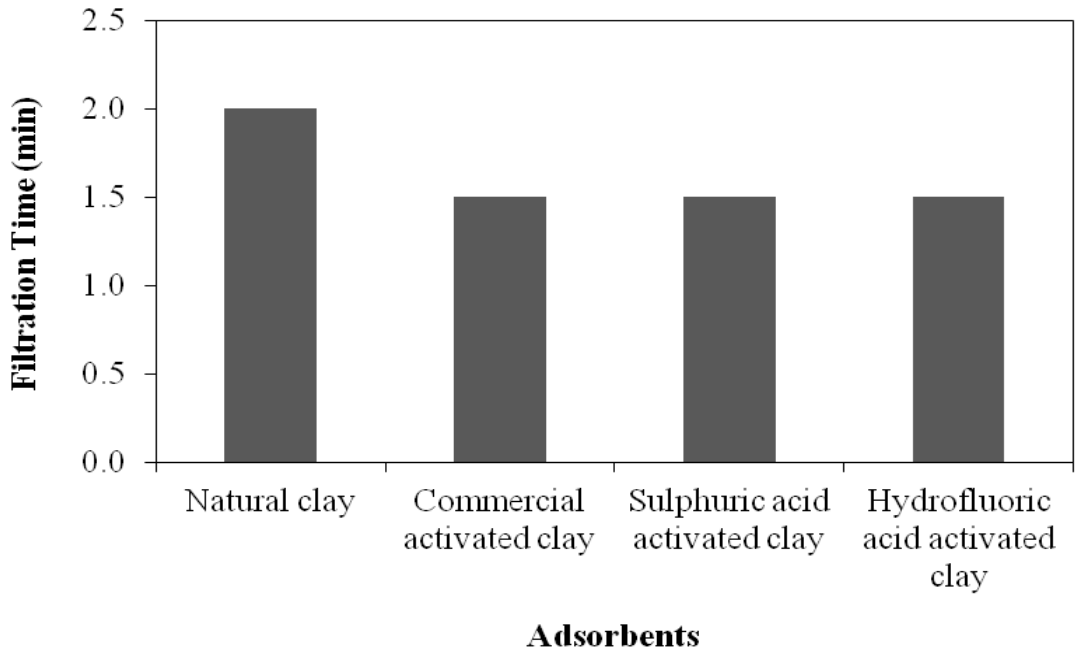


Figure 4.15: Effect of different types of adsorbent on the filtration time

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study has demonstrated that acid activated clays resulted in a more effective attack on the clays structure, represented by the decrease in the relative amount of cations belonging to the octahedral sheet and the increase in the silica oxide. Therefore, activation with sulphuric and hydrofluoric acid caused structural changes in the activated clay samples. In addition, the specific surface areas in the acid activated clays are larger than the natural clay. The specific surface areas in acid activated clays also increase by several times as the acid concentration and activation time increases. The above results revealed that clays activated with sulphuric and hydrofluoric acids play an important role in the purification of palm oil.

The bleaching performance of acid activated clays is found to be considerably better than that of the natural and commercial activated clays. The best bleaching performance obtained for clays were with 5 M H_2SO_4 and 3 M HF for 1 hour. Under these conditions, bleaching with 5 M H_2SO_4 and 3 M HF activated clays gave oils with the least free fatty acid content, peroxide value, phosphorus content as well as providing the best colour.

Besides, HF activated clay retained higher original β-carotene content compared to the natural clay, commercial activated clay and H_2SO_4 activated clay. It was interesting to observe that only 4% of the original β-carotene was lost during treatment with 3M HF activated clay, whereas, more than 23% and 27% was lost during treatment with commercial and 5 M H_2SO_4 activated clay. The results of this study have further

illustrated that clay activated with HF can claim its potential application in the purification of palm oil.

5.2 Recommendations

Based on the results, discussion and experimental data analysis done throughout this study, the following recommendations can be taken into consideration in the future studies on the performance and upgrade of acid activated clays.

a) Studies on acid activation by a mixture of both types of acid (i.e. H_2SO_4 and HF) should be conducted in order to produce the best bleaching performance with application on the palm oil industry.

b) Studies on the effect of different types of particle size distribution of acid activated clays should be carried out to determine the best particle size for acid activated clays.

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APPENDIX A

JOURNAL PUBLICATIONS

(1) Hussin, F., Aroua, M. K., & Daud, W. M. A. W. (2011). Textural characteristics, surface chemistry and activation of bleaching earth: A review. *Chemical Engineering Journal*, 170, 90-106. (*ISI-cited publication*)

(2) Hussin, F., Aroua, M. K., & Daud, W. M. A. W. (2013). The effects of hydrofluoric acid activation on montmorillonite clay in palm oil bleaching process. Submitted to *Clay and Clay Minerals Journal*. (*ISI-cited publication*)

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APPENDIX B

Characterisation of Acid Activated Clays

Table B.1: Moisture content (%) of the K-10 montmorillonite clay after treatment with H_2SO_4 and HF under different conditions

Category	Moisture Content, H_2SO_4	Moisture Content, HF
(2M-1h)	11.9	10.8
(2M-3h)	11.1	10.1
(2M-5h)	10.5	10.5
(2M-7h)	10.3	10.3
(3M-1h)	9.5	9.2
(3M-3h)	9.2	9.5
(3M-5h)	10.1	9.5
(3M-7h)	10.5	10.0
(4M-1h)	10.5	11.0
(4M-3h)	11.5	11.5
(4M-5h)	12.0	11.5
(4M-7h)	12.1	12.0
(5M-1h)	11.5	10.5
(5M-3h)	9.5	9.5
(5M-5h)	10.5	10.5
(5M-7h)	11.5	10.5
(6M-1h)	9.0	9.5
(6M-3h)	9.5	9.0
(6M-5h)	10.5	10.0
(6M-7h)	10.1	10.5

APPENDIX C

Characterisation of Bleached Palm Oil

Table B.2: Free fatty acid (FFA) content of the K-10 montmorillonite clay after treatment with H_2SO_4 and HF under different conditions

Category	FFA (%) H_2SO_4	FFA (%) HF
(2M-1h)	2.68	2.75
(2M-3h)	2.68	2.65
(2M-5h)	2.71	2.76
(2M-7h)	2.65	2.57
(3M-1h)	2.72	2.50
(3M-3h)	2.70	2.72
(3M-5h)	2.65	2.65
(3M-7h)	2.72	2.90
(4M-1h)	2.79	2.90
(4M-3h)	2.77	2.70
(4M-5h)	2.76	2.75
(4M-7h)	2.67	2.56
(5M-1h)	2.57	2.68
(5M-3h)	2.61	2.84
(5M-5h)	2.68	2.75
(5M-7h)	2.60	2.80
(6M-1h)	2.67	2.61
(6M-3h)	2.65	2.85
(6M-5h)	2.69	2.95
(6M-7h)	2.79	2.95

Table B.3: Peroxide Value (PV) content of the K-10 montmorillonite clay after treatment with H_2SO_4 and HF under different conditions

Category	PV H_2SO_4	PV HF
(2M-1h)	0.00	0.87
(2M-3h)	0.00	0.87
(2M-5h)	0.00	0.84
(2M-7h)	0.00	0.87
(3M-1h)	0.00	0.00
(3M-3h)	0.00	0.00
(3M-5h)	0.00	0.00
(3M-7h)	0.00	0.00
(4M-1h)	0.00	0.00
(4M-3h)	0.00	0.00
(4M-5h)	0.00	0.00
(4M-7h)	0.00	0.00
(5M-1h)	0.00	0.00
(5M-3h)	0.00	0.00
(5M-5h)	0.00	0.00
(5M-7h)	0.00	0.00
(6M-1h)	0.00	0.00
(6M-3h)	0.00	0.00
(6M-5h)	0.00	0.00
(6M-7h)	0.00	0.00

Table B.4: Lovibond red and yellow index after treatment with H_2SO_4 and HF under different conditions

Category	Lovibond Red Index, H_2SO_4	Lovibond Yellow Index, HF
(2M-1h)	26.5	38.7
(2M-3h)	29.6	38.7
(2M-5h)	28.7	29.6
(2M-7h)	27.1	68.6
(3M-1h)	26.5	25.0
(3M-3h)	26.5	38.5
(3M-5h)	27.5	38.7
(3M-7h)	43.5	61.5
(4M-1h)	30.3	40.2
(4M-3h)	47.6	53.6
(4M-5h)	53.3	49.9
(4M-7h)	55.5	53.7
(5M-1h)	24.4	43.3
(5M-3h)	27.5	66.5
(5M-5h)	29.8	45.0
(5M-7h)	29.8	57.5
(6M-1h)	38.3	29.5
(6M-3h)	36.3	53.5
(6M-5h)	36.3	58.5
(6M-7h)	60.6	48.5

Table B.5: Phosphorus content after treatment with H_2SO_4 and HF under different conditions

Category	Phosphorus, H_2SO_4	Phosphorus, HF
(2M-1h)	21.95	24.65
(2M-3h)	30.42	33.26
(2M-5h)	22.94	17.72
(2M-7h)	19.16	96.21
(3M-1h)	20.35	6.17
(3M-3h)	12.75	36.48
(3M-5h)	22.78	24.84
(3M-7h)	55.85	58.64
(4M-1h)	55.91	65.24
(4M-3h)	51.52	60.63
(4M-5h)	68.13	44.76
(4M-7h)	58.65	49.51
(5M-1h)	6.13	37.18
(5M-3h)	18.65	51.07
(5M-5h)	32.50	41.69
(5M-7h)	42.70	59.21
(6M-1h)	37.53	31.85
(6M-3h)	26.56	64.24
(6M-5h)	17.46	79.79
(6M-7h)	65.77	84.32

Table B.6: Carotene content of the K-10 montmorillonite clay after treatment with H_2SO_4 and HF under different conditions

Category	Carotene H_2SO_4	Carotene HF
(2M-1h)	420	524
(2M-3h)	472	528
(2M-5h)	457	527
(2M-7h)	453	534
(3M-1h)	442	523
(3M-3h)	394	534
(3M-5h)	471	531
(3M-7h)	489	530
(4M-1h)	437	520
(4M-3h)	491	530
(4M-5h)	503	548
(4M-7h)	505	532
(5M-1h)	398	546
(5M-3h)	478	532
(5M-5h)	502	528
(5M-7h)	524	536
(6M-1h)	464	538
(6M-3h)	516	524
(6M-5h)	510	523
(6M-7h)	532	528